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Waterloo Research Institute

ASSESSMENT OF WATERLOO FLASH PYROLYSIS
PROCESS TO OBTAIN LIQUID FUELS FROM
CANADIAN PEAT

FINAL REPORT

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**Assessment of Waterloo Flash Pyrolysis
Process to Obtain Liquid Fuels from
Canadian Peat**

RENEWABLE ENERGY BRANCH

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PREFACE

This report describes the first study of the pyrolysis of a Canadian peat for the purpose of obtaining a maximum yield of liquids by an economical and low capital cost process. The Waterloo Fast Pyrolysis Process (WFPP), an atmospheric pressure fluidized bed thermal pyrolysis process, was chosen for evaluation because of its success in achieving high liquid yields when biomass was used as a feedstock.

A series of pyrolysis tests at different process conditions were carried out in the small WFPP pilot plant at feed rates of 1 to 2 kg/h in order to establish optional process conditions for maximum liquid yields, and to produce sufficient quantities of pyrolysis oil to allow an evaluation of the composition of the oil. In addition, a series of tests on various grades of peat were carried out in order to evaluate the fluidized bed as a dryer for milled peat.

Few previous studies of the yields of liquids and other products obtainable from the fast thermal pyrolysis of Canadian peat have been done (Roy, 1980). Given the very large peat deposits available in Canada, and the fact that much of the resource is located where other fossil fuels are not readily available, the economical conversion of peat to a liquid fuel would have many advantages. In particular, if this oil can replace petroleum oils, e.g., for kiln firing, or can be upgraded to motor quality

fuel, then the vast peat resources can be utilized as a source of liquid fuels for future needs.

Peat is currently produced in Canada primarily for agricultural purposes and is not used as a fuel. Any of those companies currently engaged in peat production but with inadequate markets for their present production or for the lower grades of peat might find a conversion process of interest. Indeed, in this work, the cooperation of a major Quebec peat producer was of great assistance. Inasmuch as we have already reported results on the pyrolysis of lower grade (non-Canadian) peats, the higher grade Quebec sphagnum peat already being produced was chosen as the principal feedstock for this study.

The results reported here represent an initial study. They are sufficiently promising that further investigations would be warranted, particularly where short-term economic feasibility is a possibility. The production of high grade motor fuel from the peat pyrolysis oil is also a technology which should be investigated for the longer term.

ABSTRACT

Some studies on Finnish peat and Jamaican peat had shown that the Waterloo Fast Pyrolysis Process could give oil yields of 30% to 50% without operating difficulties. Accordingly, a program was undertaken to evaluate the yields of liquids and other products obtainable from Canadian peats using the Waterloo Fast Pyrolysis Process. A secondary objective was to investigate the short residence time fluidized bed as a dryer for milled peat. The pyrolysis tests were carried out in the 1 to 3 kg/h pilot plant unit developed for biomass pyrolysis, in order to yield sufficient quantities of liquid for adequate characterization.

Yields of organic liquids of about 45% to 47% of the moisture-free feed were obtained in the optimum temperature range of 450° to 550°C with a younger long fibre sphagnum peat. Char yields decreased from 35% to 26% while gas yields increased from 12% to 17% over the optimum temperature range. Carbon monoxide and carbon dioxide were the main gaseous products

The character of the liquid product changed significantly over the temperature range of 450° to 550°C, with the ratio of water soluble to water insoluble components changing from 2.3 to about 0.6, with some corresponding decrease in oxygen content. A considerable number of the individual components were identified by GC-MS.

The short residence time fluid bed dryer was very efficient when tested for four grades of Quebec peat. For all but old decomposed black peat, the bulk of the water was removed in a constant drying rate period, with critical moisture contents of about 13%. Decomposed black peat was more difficult to dry. Although these drying tests were preliminary in nature, they indicate the utility of the fluid bed unit as a dryer.

Good yields of organic liquids can be obtained from yellow or brown peats using the atmospheric pressure fluidized bed pyrolysis process. These liquids have a lower oxygen content than oils from wood, and contain some longer chain paraffinic compounds. Upgrading tests using a batch autoclave, as well as a new design of a non-isothermal continuous plug flow catalytic reactor, showed that good yields of a gasoline-like liquid could be obtained by a deoxygenation-hydrogenation process.

EXECUTIVE SUMMARY

In recent years a very successful process for the production of liquid fuels from biomass has been developed in the Department of Chemical Engineering, University of Waterloo. This process, now known as the Waterloo Fast Pyrolysis Process (WFPP) is based on atmospheric pressure, short residence time pyrolysis in a fluidized bed of sand. The reactor is designed so that biomass particles are not eluted from the bed until they are fully decomposed. This process gives the highest yields of total liquids (75% to 80% of moisture-free biomass) or of organic liquids (60% to 65%) of any thermal conversion process. Preliminary feasibility studies also indicate that the process could be one of the most economical biomass conversion processes for the production of an alternative liquid fuel. Further investigation of the liquid products has also shown that they can be a potential source of a variety of chemicals, and variation of process conditions can give some control of composition. At the present time, pyrolysis tests with the WFPP are carried out in one of two units; a bench scale continuously fed fluid bed with a feed rate of 30 to 100 g/h, or a small pilot plant unit with a feed rate of 1 to 4 kg/h.

In 1984, a complete evaluation of the pyrolysis yields obtainable from a Finnish brown fuel peat was carried out in the bench scale apparatus, under contract to the Technical Research Centre of Finland. Good yields of oil were obtained, but lack of analytical

facilities at that time did not allow evaluation of the liquid product. However, based on the success of this work, a proposal was made to the Bioenergy Development Program of Energy, Mines and Resources Canada to evaluate liquid yields obtainable from a typical Canadian peat by means of the WFPP. This program was funded in late 1985, and had three major objectives: to determine yields of liquid and other products obtainable from a Canadian peat; to use the pilot plant unit to obtain sufficient quantities of liquid product to allow some characterization to be done; and to carry out a preliminary evaluation of the performance of a short residence time fluidized sand bed with a design similar to the pyrolysis reactor as a dryer for Quebec milled peat. At a later stage of the work, it was also decided to attempt some upgrading tests of the whole pyrolysis oil to see if a higher quality fuel could be obtained.

With the cooperation of Premier Peat Moss Ltd. of Riviere-du-Loup, Quebec, four samples of Quebec peat were obtained ranging from a young high grade long fibre yellow horticultural peat to a black highly decomposed old peat. Drying studies were done for all of these peats, and detailed evaluation of pyrolysis yields, and characterization of liquid products was done for one of the younger peats and for the oldest peat. The pilot plant unit at feed rates of 1.2 to 2.0 kg/h was used in all tests.

For the three younger peats, drying in the fluidized sand bed at bed temperatures of 89° to 137°C took place largely in the constant rate period with critical moisture contents of 0.13 to 0.15 kg water/kg BD peat, starting with initial moisture contents of up to 0.8 kg water/kg BD peat. Constant drying rates for these peats varied from 0.5 to 0.8 kg H₂O/(kg dry peat)(min). The black peat had a higher initial moisture (1.2 kg/kg) and a higher critical moisture content (0.37 kg/kg) as well as a somewhat higher constant drying rate (1.0 kg/kg min) than the younger peats. Because the evaporation temperature in the constant rate period must be close to the adiabatic saturation temperature, the peat particles are not overheated in the constant rate period and any irreversible structural changes resulting from drying should be minimized. Concurrent drying tests carried out by thermogravimetry showed that much valuable qualitative information concerning the drying rate behaviour of the peat can be gained rapidly by this technique. There was a high degree of correlation between the observed drying rate behaviour in TGA tests and in the pilot plant fluid sand bed. At steady state operation, good heat balances (±5%) were obtained for the fluidized bed dryer.

Pyrolysis tests on a Quebec Sogevex peat were carried out in the range of 450° to 559°C. Total liquid yields of about 57% by weight of the moisture free feed, and organic liquid yields of 45% to 47% were obtained over an optimum temperature range of 450° to 550°C. Liquid yields decreased to 25% at 692°C. Char yields

decreased from 35% to 25% from 450° to 550°C and then became constant. Gas yields increased steadily from about 12% at 450°C to 37% at 690°C. From these results, it is apparent that the decrease in organic liquid yields at temperatures above 550°C resulted in a corresponding increase in gas yields. The major gas products (80% to 90% by weight) were CO and CO₂. The CO₂ increased from 8% to 10% from 450° to 550°C and then became constant, whereas the CO increased continuously from 3% to 22% over the temperature range of 450° to 770°C. Hydrocarbon gases increased continuously with temperatures from about 0.4% at 450°C to 7.0% at 692°C.

One of the most interesting results of this study concerns the nature of the organic liquid product obtained in the optimum temperature range. As temperature increased from 450° to 550°C, the weight ratio of water soluble components to water insoluble components in the organic liquid product changes from 2.3 to about 0.6 while the organic liquid yield remained virtually constant. Above 550°C, the water soluble/water insoluble ratio showed much less change as temperature increased. This decrease in the yield of water soluble compounds was accompanied by a decrease in oxygen content from about 39% to 34% although the molal H/C ratio of the tar remained approximately constant at 1.5.

Detailed quantitative characterization of the water soluble fraction of the organic liquid product showed that the components present and their amounts were typical of the product of

carbohydrate pyrolysis normally obtained with the WFPP. At low temperatures (450°C), a much larger proportion (about 50%) of the water solubles was sugars, mainly levoglucosan, while at 690°C less than 20% was sugars. The relatively high yield of levoglucosan is surprising (6% to 8% of peat fed), since the peat contained only about 20% cellulose, and this high value is in contrast to wood (48% cellulose) which normally in the WFPP would yield only about 1% levoglucosan.

Analysis of the water insoluble fraction of the tar and of the hexane and toluene soluble fractions of the tar by GC-MS allowed qualitative identification of a large number of compounds. A number of long chain paraffinic compounds were obtained, as well as aromatic compounds derived from the sphagnol portion of the peat. These latter "lignin" derived substances are substituted hydroxy benzenes, low in methoxy content. Tentatively, it could be concluded that the tar from peat might be a better feedstock for upgrading to high quality fuels than is pyrolytic wood oil.

Variation of moisture content of the peat feed up to 30% by weight did not affect the yields or composition of the organic liquid product in the optimum temperature range. Similarly, a more than twofold change in feed rate (0.86 to 2.01 kg/h) did not significantly affect product yields or compositions. Vapour residence time was not varied by more than 20%, but there was little effect within this range.

Thermogravimetric analysis of the various peats gave volatile yields which correlated qualitatively with the results of bench scale and pilot plant pyrolysis tests. TGA would, therefore, be a useful initial analysis for an unknown peat feedstock, yielding meaningful results for workers with prior experience in the pyrolysis of various peats.

The results obtained from the pyrolysis of the Sogevex Quebec peat were entirely comparable to the results obtained in our laboratory for the Finnish brown fuel peat using the bench scale unit.

Pyrolysis tests were also carried out on a black fuel grade Quebec peat (Premier peat). Yields of char were higher by 3% to 5% than for brown peat, and gas yields were about 2% lower, although the trends with temperature were parallel for the two peats. Organic liquid yields at the optimal temperature of 500° to 550°C were about 40% for the black peat compared to 47% for brown peat. The ratio of water insoluble to water soluble components in the organic liquid showed a similar increase with temperature to that found for the brown Sogevex peat. Analysis of liquid components showed a surprising correspondence of the two pyrolysis tars. In general, although organic liquid yields were somewhat lower for the black peat compared with the brown peat, the fast pyrolysis results were remarkably similar for the two feeds considering the difference in quality of the two peats.

Upgrading studies of the WFPP peat oil were carried out originally in a batch autoclave. However, the thermally sensitive nature of pyrolysis oils requires a special non-isothermal hydrogenation-deoxygenation sequence which is difficult to achieve in a batch system. A small continuous plug flow catalytic reactor was developed which could be made to operate with the required axial temperature gradient. Upgrading tests of the peat oil in this reactor finally yielded quite satisfactory results using a sulfided nickel-molybdenum on alumina catalyst at 240° to 380°C and 13.7 MPa. The liquid product was a gasoline-like material with a yield of about 39% of the tar fed.

In conclusion, the original objectives as well as secondary ones of the present contract have all been satisfactorily met. The upgraded light hydrocarbon liquid obtained from peat oil should be tested for fuel quality. Depending on these results, a more extensive series of upgrading tests may be warranted.

Quantitative measurements of the amounts of long chain paraffinic compounds available in the oil should also be carried out, to evaluate whether or not it is worthwhile to recover this group of compounds from the pyrolytic oils.

From a process viewpoint, no problems were encountered with continuous operation of the WFPP on brown or yellow peats, long or short fibred, at moisture contents to 30%, nor on black peat at moisture contents to 39%. The production of a substitute fuel oil

from peat has certain advantages - a transportable and storable energy source of high energy density, and the advantages of an ash-free liquid fuel feed over a low density solid feed. Excess char could be pulverized and blended with the oil if desired to obtain higher calorific values: such fuels might fill a role for special purposes, such as the firing of lime kilns.

The selling price of a pyrolytic oil from peat should be comparable to that estimated when using waste wood as a feedstock (\$5 to \$6 per million BTU). The lower oil yield is offset by a higher calorific value of the oil. Plant size can be larger for peat pyrolysis than for biomass pyrolysis because of the availability of raw material at a single site in the case of peat. It is probable that at some locations in Canada, remote from other fossil fuel sources, the production of peat oil as a fuel could be economically viable in the very near future. A preliminary economic feasibility study is needed to assess the costs of upgrading the crude peat oil to transportation grade fuel when more data is available on operating parameters and fuel quality.

ASSESSMENT OF WATERLOO FLASH PYROLYSIS
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1. INTRODUCTION

Twelve percent of the land area of Canada can be classed as peatlands. Therefore, peat represents a very large fuel resource for Canada's future energy needs. However, at the present time, peat in Canada is produced almost exclusively for horticultural or other agricultural uses. A substantial fraction of this production of about 0.75×10^6 tonnes per year is exported.

Most of the available up-to-date information on Canadian peat resources and their potential for future use is available as a result of a National Energy Program established in 1982, managed by the National Research Council until 1985 when the program was terminated. However, during this period a considerable number of studies were completed which covered resource inventory, classification, mining methods, experimental production technology, de-watering studies and various environmental studies, and which represent the best current information on Canadian peatlands and on the technology of peat production and utilization. (We are indebted to Dr. R.P. Overend of the National Research Council of Canada, Division of Energy, for supplying to us a complete file of reports of studies carried out under this program.)

However, it is interesting to note that only one pyrolysis study (Roy, 1984) of a Canadian peat for the purpose of obtaining maximum liquid yields has previously been reported, although numerous studies by workers in other countries have used peats as feedstocks, primarily for combustion or gasification tests. In our laboratory, we have carried out bench scale pyrolysis tests on a low grade Jamaican peat (Scott et al., 1985a), and an extensive series of bench scale tests on a Finnish fuel grade peat (Scott et al., 1985b). In the latter work, the Waterloo Fast Pyrolysis Process was used, and the primary objective was the determination of optimum pyrolysis conditions for a maximum yield of organic liquids.

On October 31, 1985, financial support was received from the Bioenergy Development Program of the Renewable Energy Division of Energy, Mines and Resources Canada to conduct an assessment of the Waterloo Fast Pyrolysis Process as a means of producing oils from peat. This study was to be carried out in our larger pilot plant facility in order to recover sufficient quantities of liquid for characterization.

Peat is a general term which covers a very wide range of biomass materials in various stages of decomposition, occurring in a variety of environments. The characteristics of peat can vary from a near-lignite, semi-colloidal black highly humified material, to moderately or slightly decomposed grasses and mosses (brown or yellow peat). The peats currently produced in Canada

are high moor, younger peats, used mainly in horticultural work. Very little of the more decomposed fuel grade peat is produced. Excellent reference works and reviews on peat are available, for example that of Chornet, and it is not an objective of this work to assess peat qualities, or present or potential uses.

Experimental work for the present study did not commence until the latter part of March, 1986, due to a delay in obtaining samples. However, with the cooperation and considerable assistance of Premier Peat Moss Ltd. of Rivière-du-Loup, Québec, we were able to obtain adequate supplies of four types of peat available in that province. Two of these were from deposits presently in commercial production by Premier Peat Moss Ltd. Liaison with this company has been maintained throughout this work.

In conclusion, this study represents the first attempt to apply fast pyrolysis, specifically the Waterloo Fast Pyrolysis Process, to Canadian peats, with the objective of recovering maximum yields of liquid, and evaluating these liquid products. The benefits of converting peat to a more desirable fuel are the same as for biomass conversion. The oil is a much more volumetrically dense energy form, and is more easily transported and stored than dry or moist peat. The residual char can be gasified or burned, as it is a very reactive solid fuel. A blended mixture of finely ground char and peat oil could give a stable high energy liquid fuel which could be easily transported and stored. The gas has a

sufficient heat content so that it could be used to supply a good part of the energy requirements of the process.

Inasmuch as the raw material harvesting problem that exists with normal biomass, and which may limit the size of a biomass pyrolysis plant, does not exist for peat, large plant sizes can be considered, with the resulting economies of scale.

Given the large reserves of Canadian peat, much of it located in Eastern Canada where there is little alternative fossil fuel available, it would appear to be wise to develop a technology for use of these peat deposits for energy production, and as a source of hydrocarbons or petrochemicals. This study is a contribution to the development of such technology.

2. OBJECTIVES

To our knowledge, no fast pyrolysis studies of Canadian peats for the primary objective of producing a maximum liquid yield have previously been carried out. Therefore, the present work represents a preliminary assessment study of the potential value of the Waterloo Fast Pyrolysis Process (WFPP) for the production of liquid products from peat. As discussed in the previous section, the WFPP has been used with a Finnish Carex peat, with promising results.

Accordingly, the major objective of the present work was to evaluate a number of aspects of the WFPP as applied to a typical Canadian peat, principally:

1. To carry out drying tests in a fluidized bed to allow quantitative evaluation of drying rates, primarily to obtain actual performance data for these peats;
2. To investigate the effect of process operating variables on the yields of pyrolysis liquids from Canadian peat, if possible using two or more feedstocks. The small scale pilot plant was to be used at feed rates of 1 to 3 kg/h to obtain reasonable amounts of liquid products for evaluation;
3. To evaluate the nature of the pyrolytic liquids obtained at different process conditions by measurement of chemical and physical properties on selected samples.

All of the above objectives were achieved, and the determination of yields of liquids and characterization of the liquid product was carried out in detail for one medium grade peat.

3. METHODS AND PROCEDURES

3.1 Apparatus

The tests carried out in this work were all done in the small scale fluidized bed pilot plant unit, with a feed rate of up to 3 kg/h. This apparatus and its method of operation has been described in detail by Scott and Piskorz, 1984 and Scott and Piskorz, 1985. A schematic flow sheet of the pilot plant is shown in Figure 3.1, and the construction of the fluidized bed reactor is given in Figure 3.2. Data for the reactor are given in Table 3.1.

Briefly, the peat or biomass was metered by a twin screw feeder and then fed to the atmospheric pressure fluidized bed of sand in an entrained gas flow. The necessary heat for pyrolysis was supplied by preheating the metered fluidizing gas. About 15% of the total inlet gas flow was used to entrain the feed. The apparent gas residence time was from 0.35 to 0.7 seconds, defined as the net reactor volume divided by the total inlet gas flow rate at reactor conditions. The gas flow rate, and sand and feed particle sizes, were selected so that the sand or the peat feed was not eluted from the bed, but the low density char formed after pyrolysis was conveyed out of the reactor into the cyclone. In effect, the residence time of the solid feed was several seconds, that is, the time required to produce a

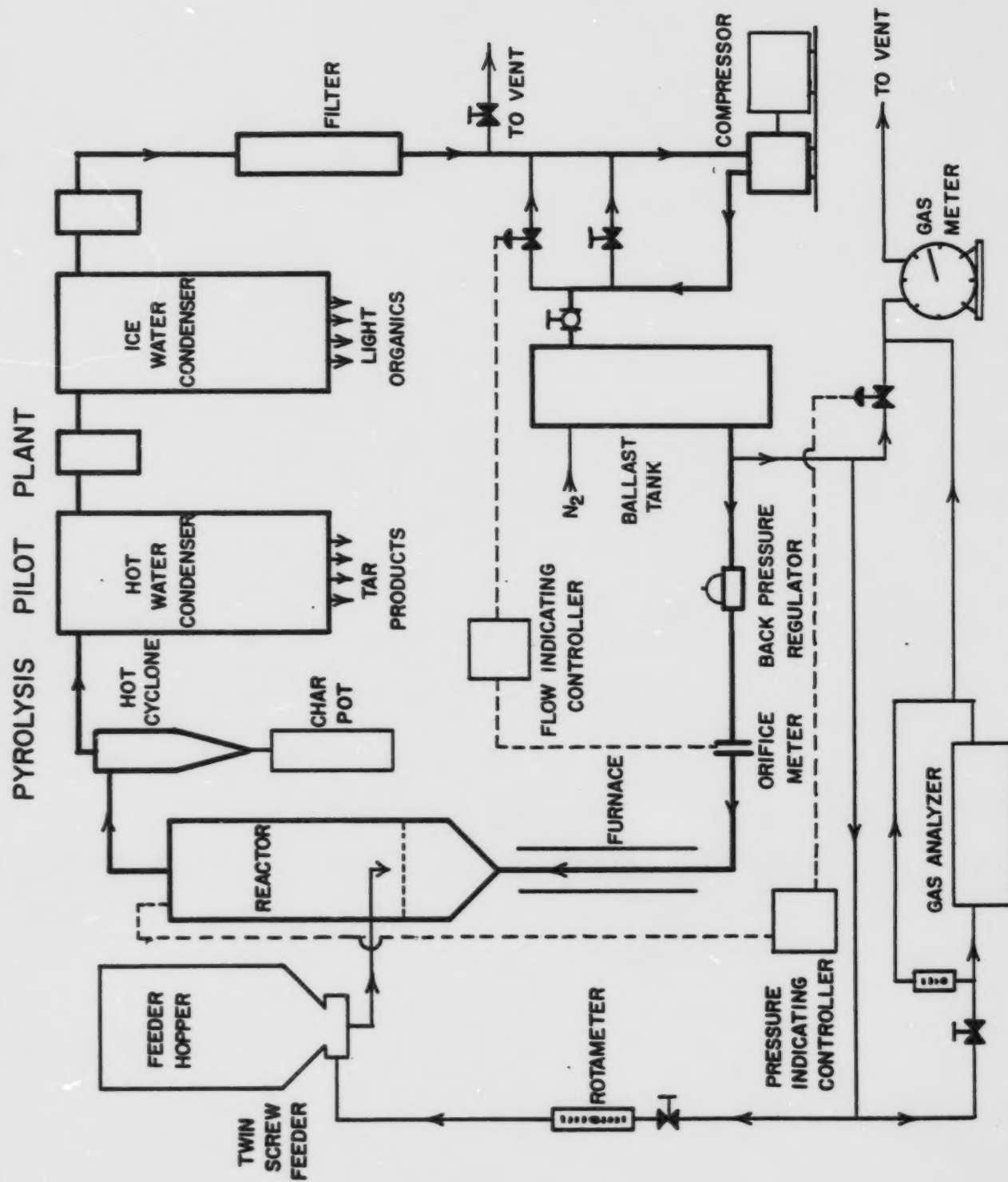


Figure 3.1 Fluidized Bed Pyrolysis Reaction System

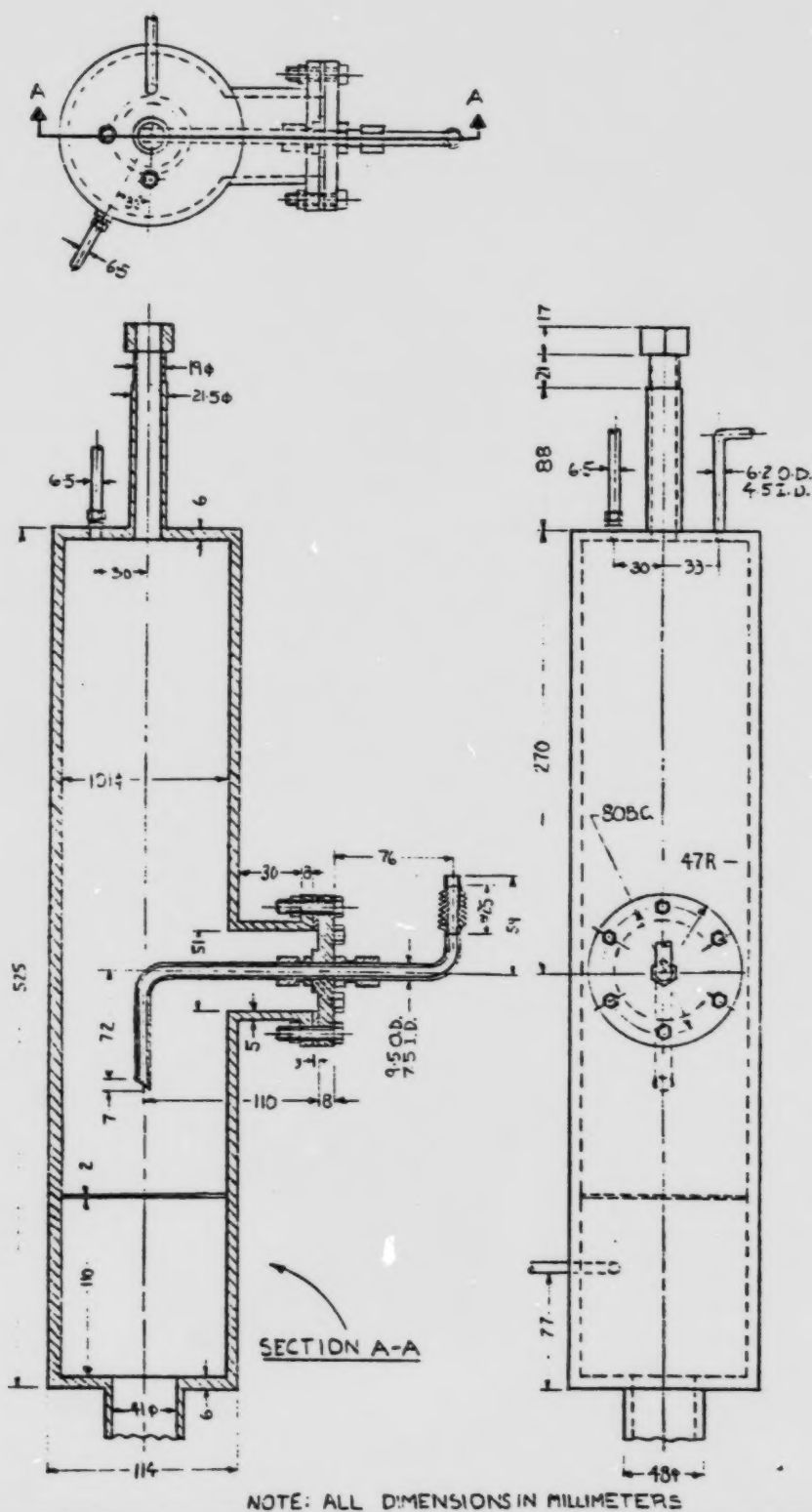


Figure 3.2 Detail of Fluid Bed Pyrolysis Reactor

Table 3.1

Fluidized Bed Reactor

Technical Data - Drying Tests

Diameter	4", (10.08 cm)
Height	40 cm
Volume	3.19 liters

Fluidized bed medium - Ottawa Sand

-20, +30 mesh (0.59-0.84/mm), density 2.47 g/cc	
Amount of sand in the bed	1800 grams
Net volume of the reactor	2.46 liters
Static depth of sand in the reactor	13.9 cm
Min. Fluidization Velocity (1 atm)	0.30 m/s

Fluidized bed ReactorTechnical Data - Pyrolysis Test
(Runs 88, 89)

Diameter	10.08 cm (4 inches)
Height	40 cm
Volume	3.19 litres
Fluidized Bed Medium	Ottawa Sand -20 +30 mesh (0.59-0.84 mm) density 2.47 g/cm
Amount of Sand	2100 grams
Net Volume of the Reactor	2.34 litres
Static Depth of Sand in the Reactor	16.5 cm

low density char. This method of operation also applied to drying tests, in which peat was retained in the sand bed until the density of the dry peat was sufficiently low to allow elution from the reactor to occur. This also gave a self-regulating, but not precisely known, solid residence time in the drying tests.

The condensable vapours formed were collected in two vertical tube surface condensers in series, the first kept at 50° to 80°C and the second at 0° to 10°C. Because of the formation of tar fogs on cooling, filters were also necessary before the recycle compressor. The fluidizing gas and the feed entrainment gas were recycled product gas.

Further details of the operating procedures for the pilot plant unit can be found in the references cited above. Specific procedures for drying tests and for pyrolysis tests are given in the succeeding sections.

3.2 Materials Used

Some delay was experienced in finding a source of Canadian peat which would allow us to have access to the expertise of a major producer. Although this caused several months delay in the initiation of this work, the benefits of the collaboration with Premier Peat Moss Ltd. of Rivière-du-Loup have been of great value to us. The original contract commencement date was October 30, 1985, and samples of peat moss suitable for the proposed study arrived in our laboratory in March, 1986.

The peat samples supplied through the cooperation of B. Belanger of Premier Peat Moss Ltd. (C.P. 482, Rivière-du-Loup, Québec G5R 3Z1) arrived in Waterloo on March 4, 1986. The following are amounts and kinds of samples received:

- | | |
|---|---------------|
| 1. NAMSCO - sphagnum peat moss | 12 cubic feet |
| 2. Premier "PIT MOOSE" - sphagnum peat moss | " |
| 3. PREMIER PEAT MOSS - sphagnum peat moss | " |
| 4. SOGEVEX - yellow sphagnum peat moss | " |

All the above peats were delivered in the compressed form and quite wet with a moisture content above 50% by weight. Data on the source and grade of these peats (as supplied by R. Leclerc of Premier Peat) are given in Table 3.2.

For preliminary drying and pyrolysis tests SOGEVEX yellow sphagnum peat moss was chosen because it is representative

Table 3.2

<u>Name</u>	<u>Origin</u>	<u>Level of Degradation</u>	<u>Colour</u>
1. Premier Peat	Rivière-du-Loup	high	black
2. Namsco	Rivière-du-Loup	medium	brown
3. Sogevex	Baie-Comeau	low	yellow
4. Pit Moose	Pointe-au-Père	very low	blond

Table 3.3

Sogevex Peat - Screen Analysis

Oven Dried Peat (105°C, 4 hours), 20 min. screen time

<u>Size Fraction</u> [mm]	<u>Weight %</u>	<u>Tyler Mesh Size</u>
Above 1.7	0.13	+10
0.85 - 1.7	4.82	10 - 20
0.59 - 0.85	8.09	20 - 28
0.425 - 0.59	15.94	28 - 35
0.30 - 0.425	20.06	35 - 48
0.15 - 0.30	23.96	48 - 100
Below 0.15	26.99	-100
	99.99	

of the grade of peat currently being produced in Canada. Six cubic feet of this peat were decompressed and reduced in size to $-590\text{ }\mu\text{m}$ using a Brickmann cutting mill model SM 1. After oven drying for 4 hours at 105°C , a sample of this peat was screened with results shown in Table 3.3.

More detailed characterization of the peat is given in the next section.

The ash content of peat was determined by combustion at 700°C in a porcelain crucible. The average of three determinations was used.

Moisture content of peat was determined by oven drying in air at 105°C for four hours. It is recognized that some volatile or thermally unstable components of peat in addition to water may be lost also during the drying. However, this method was used uniformly for all samples.

Details of other analytical procedures are given in appropriate sections.

3.3 Feeding of Peat

A calibration of the twin screw feeder in the pilot plant is shown in Figure 3.3, as feed rate of disintegrated Sogevex peat in grams per hour versus setup of potentiometer (proportional to screw RPM). The feed rate was different

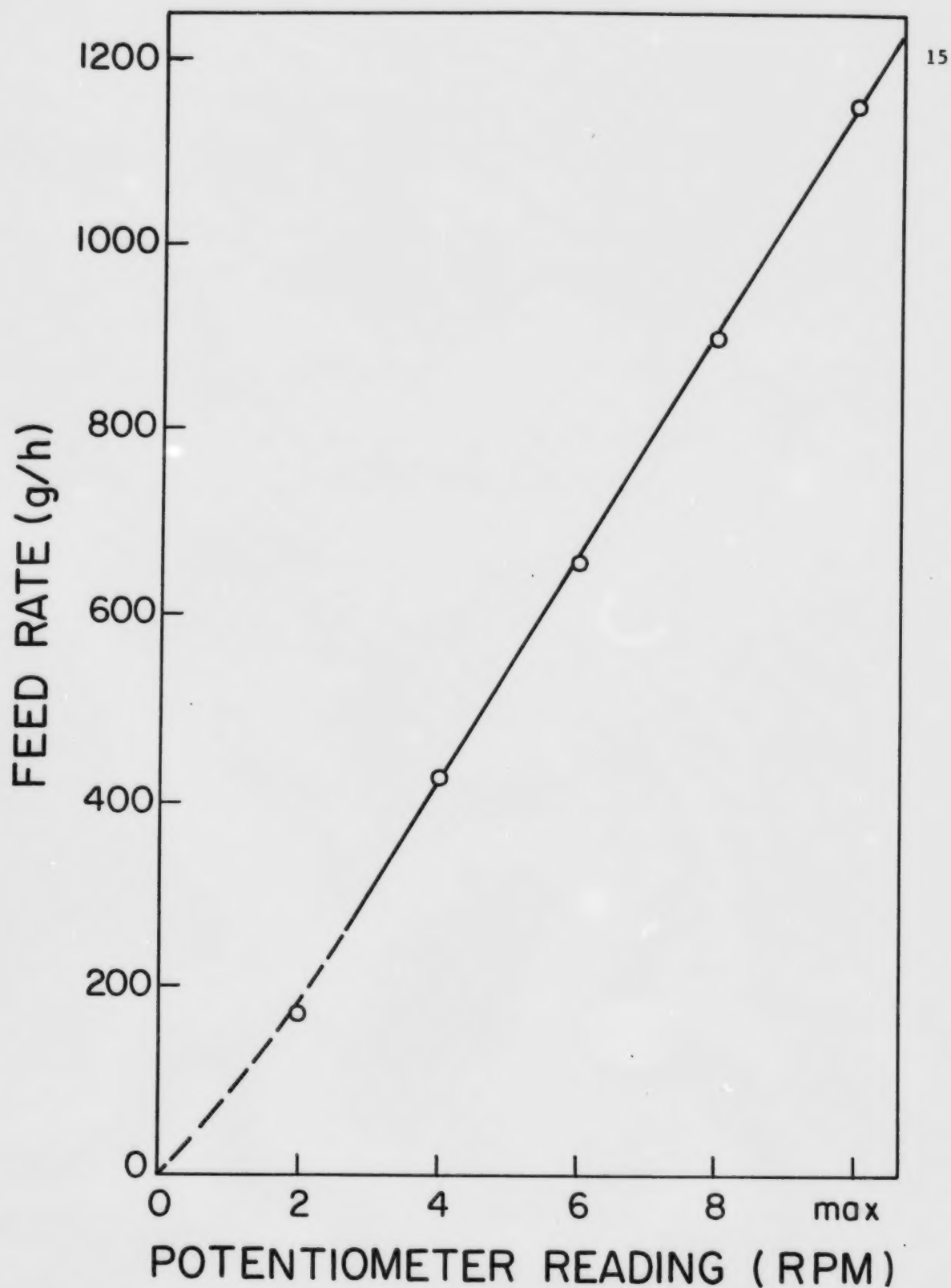


Figure 3.3 Screw Feeder Calibration for Wet Sogevex Peat

for moist and for dry peat, and hence a special calibration was required for moist peat.

Additional information for these feeding tests is given below:

(a) absolute moisture content of peat used

range - 0.70 to 0.90 $\frac{\text{kg water}}{\text{kg dry peat}}$

(b) flowrate of air - 15 liters/min, 21°C

(c) Fluidized bed 10 cm diameter x 40 cm high contained
1800 grams of sand

(d) wetness of peat used was not very uniform.

Maximum obtainable feed rate was about 1100 g/h, or 18 g/min. This maximum feed rate is equivalent to about 500 g of water plus 600 g of dry peat per hour, assuming a moisture content of 0.8 kg/kg. At this maximum feed rate, some sporadic blockages took place.

4. RESULTS AND DISCUSSION

4.1 Drying of Peat

4.1.1 Preliminary Drying Tests by TGA

To get some indication of the drying rate phenomenon of the Sogevex peat chosen for detailed testing, thermogravimetric measurement was attempted using a Perkin-Elmer TGS #2 analyzer at isothermal conditions. Recorded weight loss curves obtained during the isothermal heating up of samples are shown in Figure 4.1, and represent the rate of removal of moisture with time. Constant weights of samples were achieved in

8 to 10 minutes at 60°C

2.5 to 3 minutes at 100°C

1.5 to 2 minutes at 150°C.

Changing the flow of nitrogen from 45 ml/min to 90 ml/min did not have any visible effect on the curves presented in Figure 4.1.

The TGA analysis does not simulate exactly the conditions which would exist in a fluidized bed reactor. However, one can expect that the water removal process in a well designed fluidized bed system would be no slower than during TGA analysis.

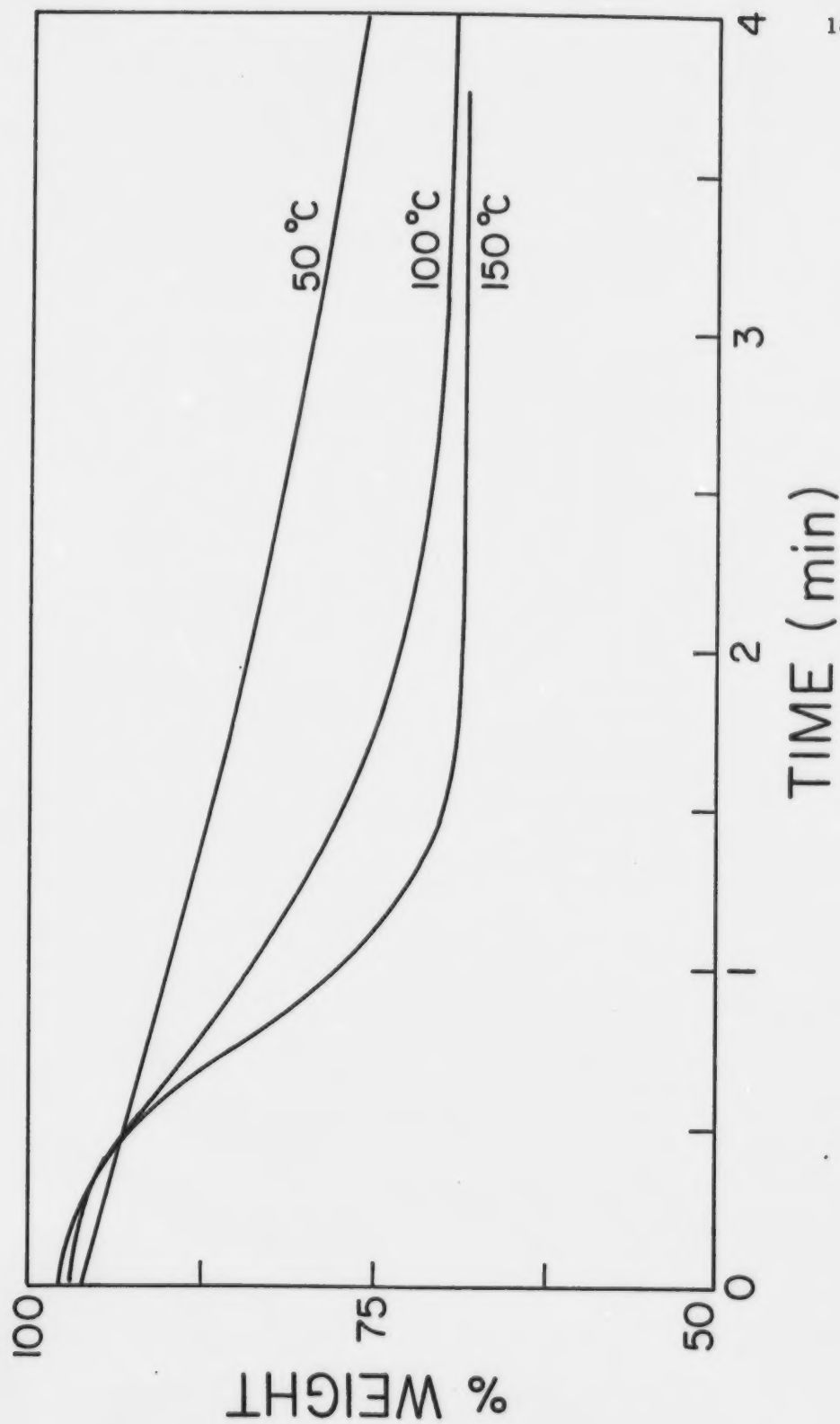


Figure 4.1 TGA Drying Rate Curves for Sogevex Peat- Effect of Temperature
-590 μm , N_2 at $45 \text{ cm}^3/\text{min}$, 7 mg sample

The data shown in Figure 4.1 were replotted in Figure 4.2 on a dry basis, that is, kg water/kg bone dry peat. An approximate differentiation of the weight loss curve is also shown in Figure 4.2, and a constant rate period of drying and a falling rate period are clearly evident. The critical moisture content of 0.13 kg water/kg BD peat (11.5% by weight) suggests that at these relatively slow drying rates sufficient drying prior to pyrolysis would be in the constant-rate period. Drying below 30% moisture is not necessary, but is desirable for ease of feeding and for energy efficiency in the overall process. In fluidized bed drying a higher critical moisture content is expected.

Because of the clearly defined drying rate behaviour observed with the TGA technique, all the peat samples were subjected to this analysis in order to evaluate the nature of the water removal process from these peats of different grades under simulated drying conditions.

Results are presented in Figures 4.3 to 4.6 and summarized in Table 4.1. Conditions adopted for all measurements were,

temperature	-	150°C isothermal
flow	-	45 cc/min, Nitrogen
sample size	-	4 to 7 mg.

Small samples of approximately 10 grams of all peats were left at room conditions for 12 days to allow "natural"

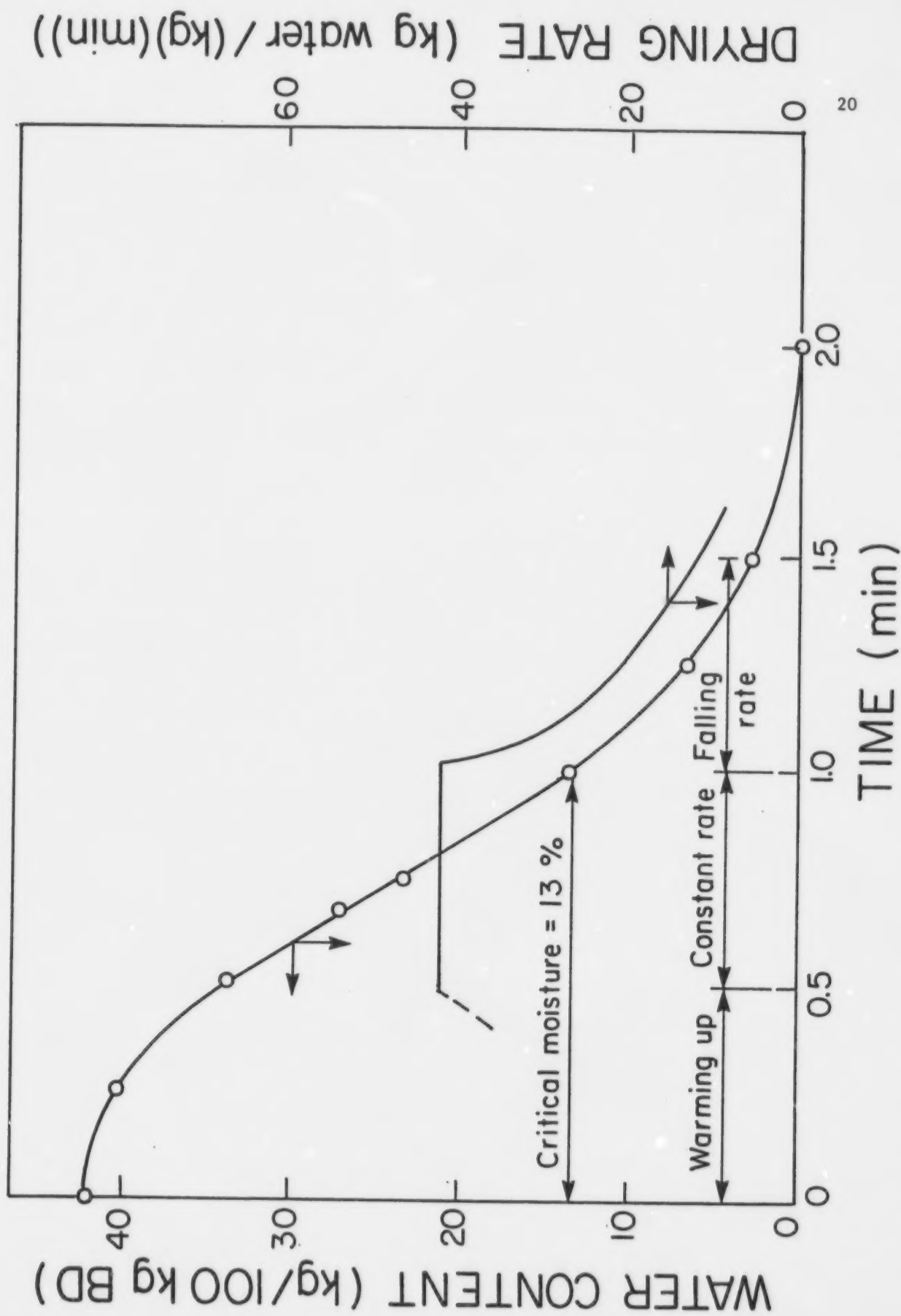


Figure 4.2 TGA Drying Rate Curves for Sogevex Peat, 150°C

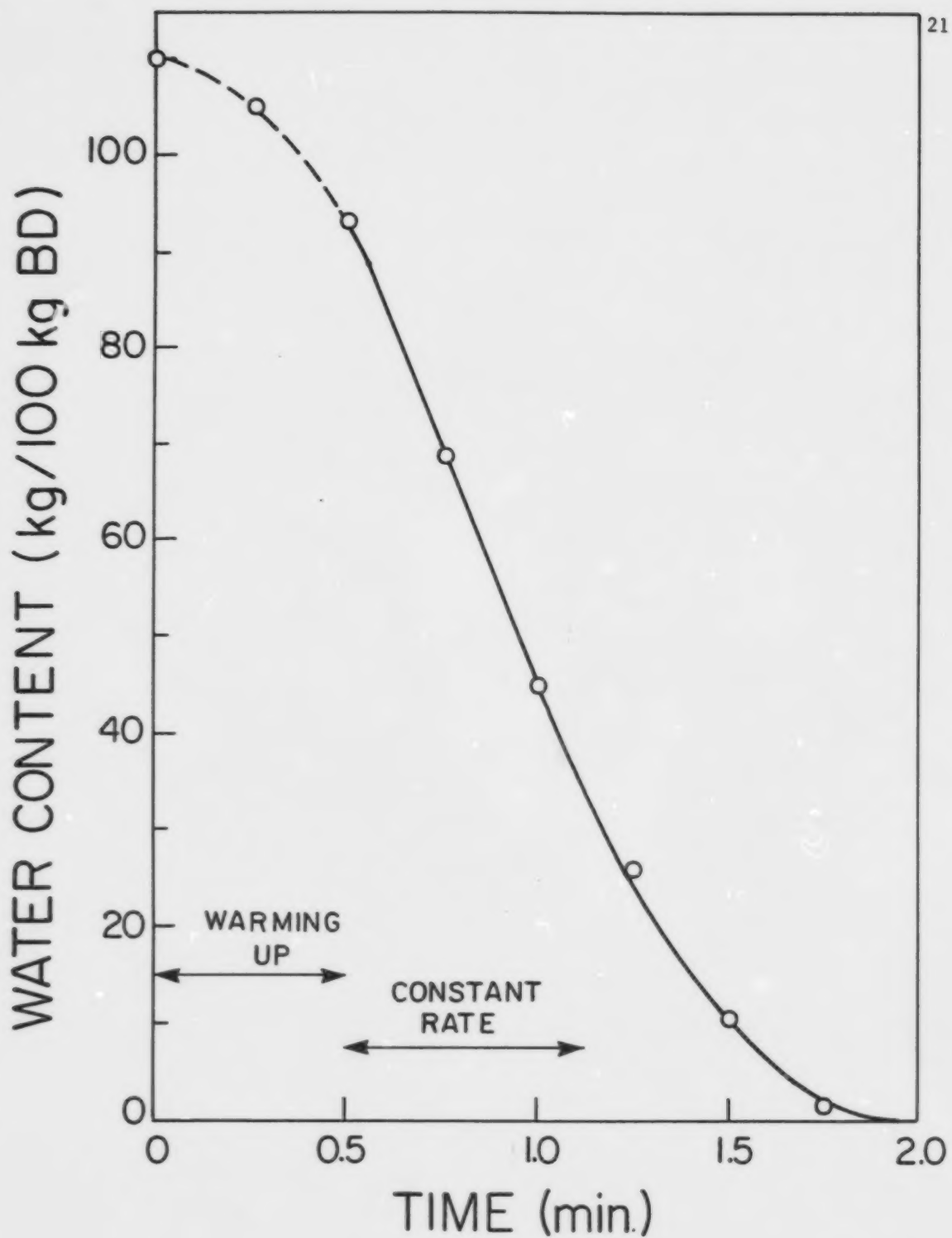


Figure 4.3 TGA Drying Curves for Premier Peat, 150°C

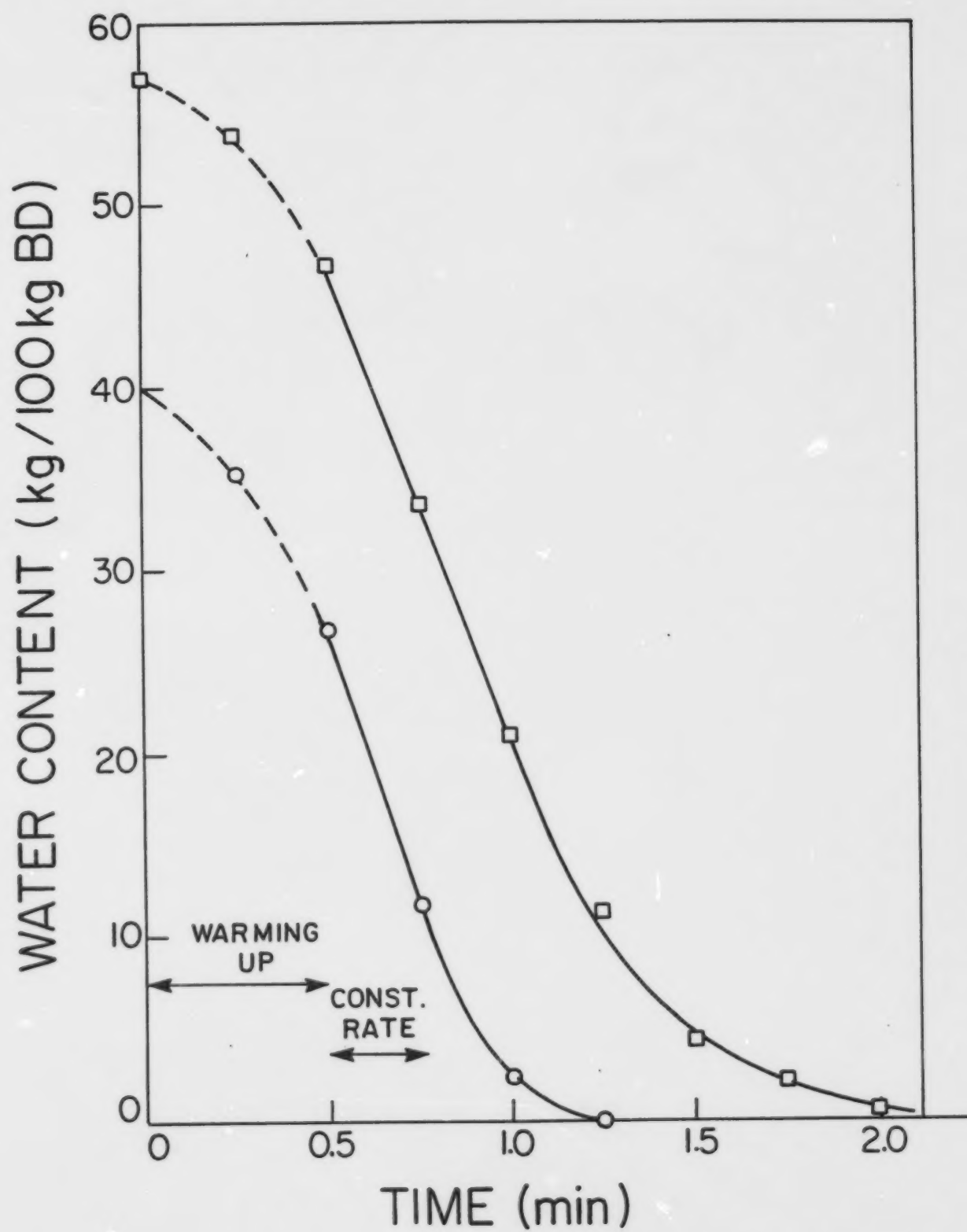


Figure 4.4 TGA Drying Curves for Namsco Peat, 150°C

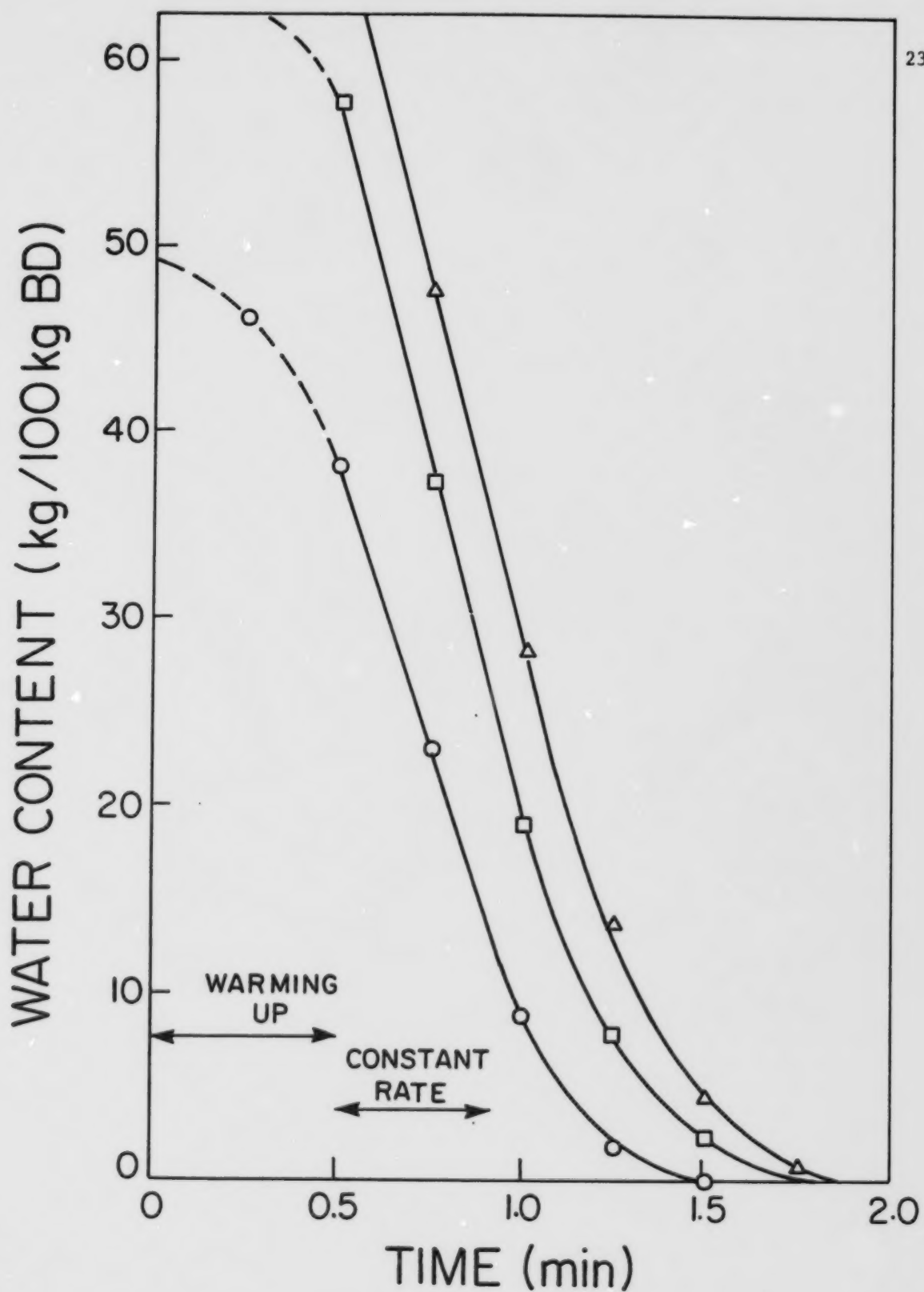


Figure 4.5 TGA Drying Curves for Sogevex Peat - Effect of Different Initial Moisture Contents, 150°C

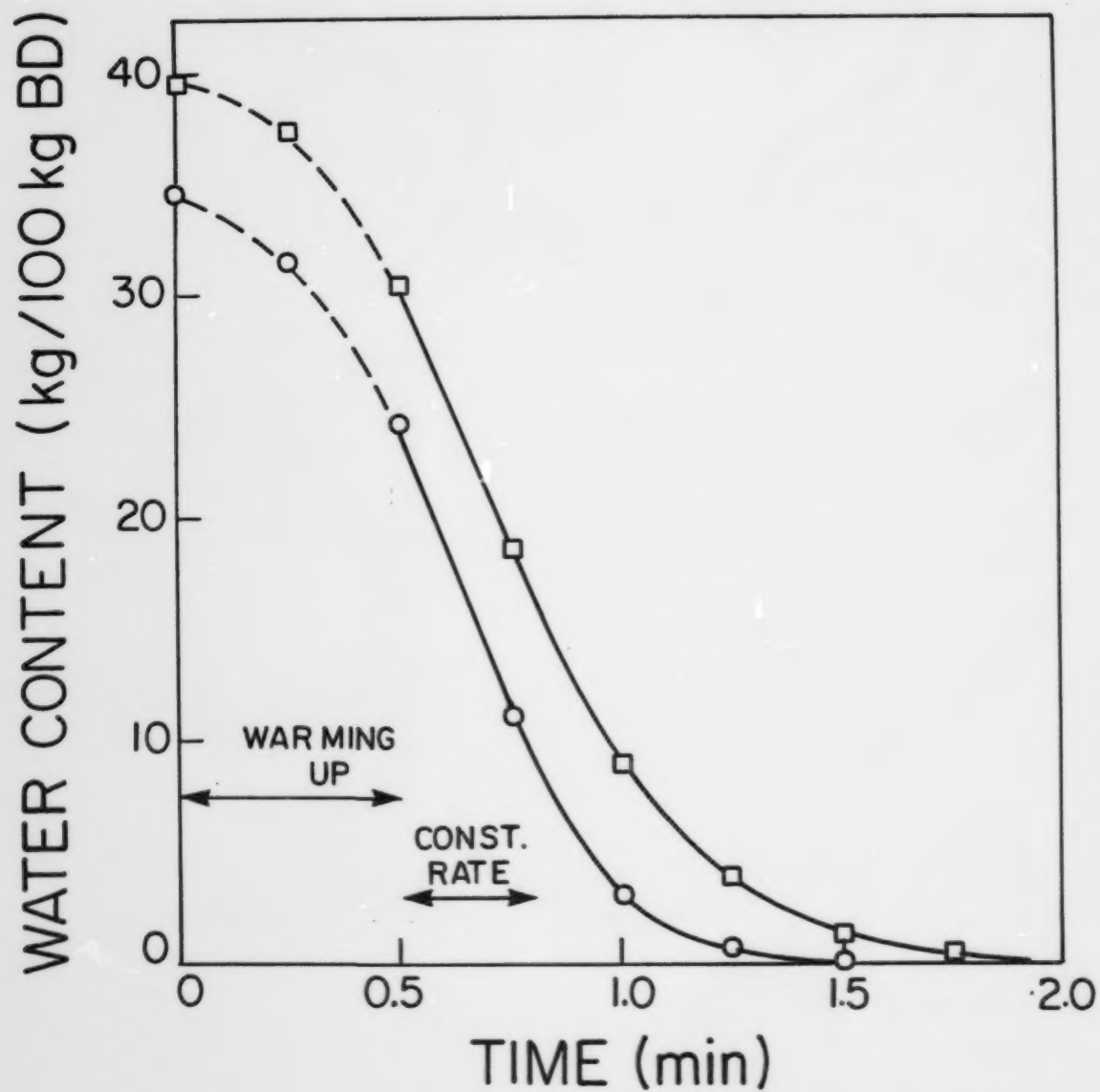


Figure 4.6 TGA Drying Curves for Pit Moose Peat - Effect of Different Initial Moisture Contents, 150°C

Table 4.1

Constant Rate Drying of Peats

Name	Critical Moisture [kg water/kg BD peat] x 100	Drying Rate in Constant Rate [kg/kg min]	Initial Water Content [kg water/kg BD peat]
1. Premier Peat	37 $\pm$ 5	1.0	1.2
2. Namsco	13.5 $\pm$ 2.5	0.6	0.55
3. Sogevex	15 $\pm$ 2.5	0.8	0.70
4. Pit Moose	12.5 $\pm$ 2.5	0.5	0.40

Table 4.2

Equilibrium Water Content with Ambient Air

Name	Water Content [kg H ₂ O/kg peat] x 100
1. Premier Peat	14.5
2. Namsco	14.9
3. Sogevex	13.9
4. Pit Moose	14.4

Determination done using drying oven @ 105°C

evaporation of water. The equilibrium water content of peats with air are presented in Table 4.2.

The water content in equilibrium with ambient air shows little difference among the various peats, old or young. However, the critical moisture content, W_c (the moisture content at which the constant drying rate changes to a falling rate) is much higher for the more decomposed black peat than it is for the younger brown peats, which all show about the same value of W_c , a value which is also about the same as the "equilibrium" moisture. This result suggests that most of the water removal in the younger peats is all by a similar mechanism, but that the old decomposed peat has more of the water content strongly bound to the organic matrix. Figures 4.3 to 4.6 also show that the great bulk of the water contained in the peat is removed in a constant rate period, and is therefore, presumably capillary water.

4.1.2 Peat Drying in a Fluidized Bed

A number of tests were carried out using the Sogevex peat as feed to determine the range of satisfactory operating conditions of the fluid bed for good drying performance. A schematic representation of conditions used is shown in Figure 4.7. The results of nine experiments carried out are shown in Table 4.3.

Figure 4.7

Schematic Presentation of Streams
Involved in the Process of Peat Drying

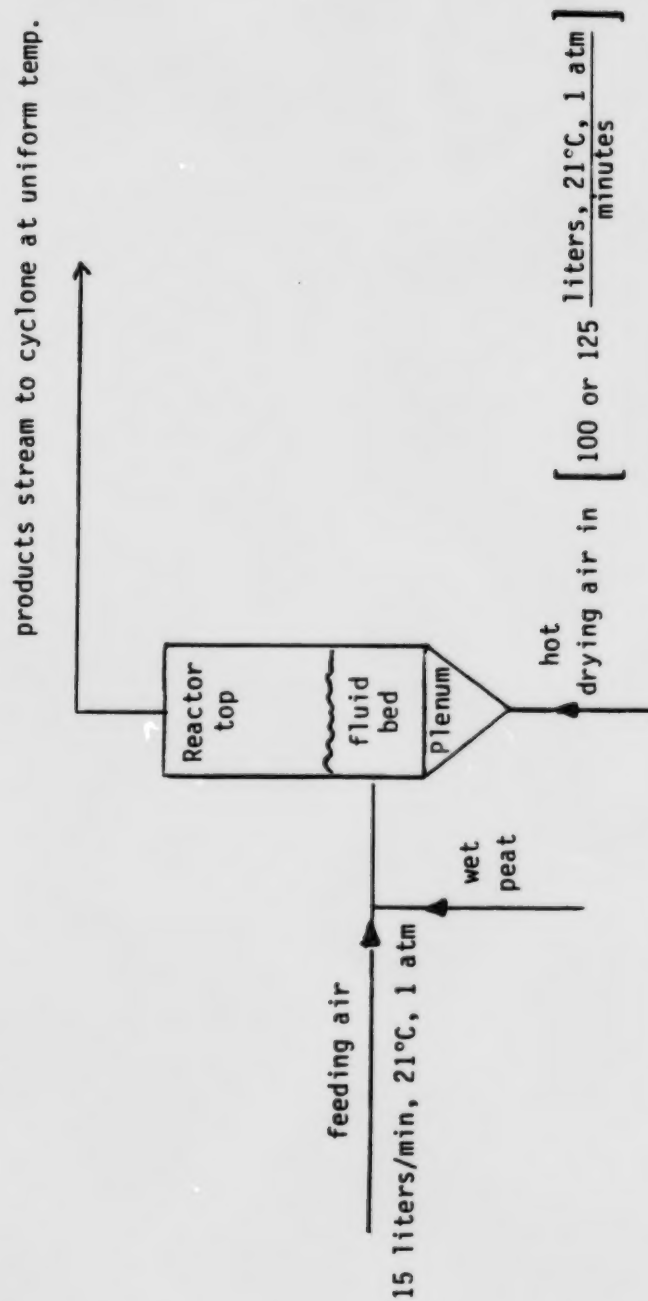


Table 4.3

Preliminary Drying Experiments*

Run #	5	6	7	9	10	8	2	3	4	1
	Temperature, °C									
Plenum Chamber	166	190	219	236	235	232	245	278	333	163
Fluid Bed	139	150	177	124	117	119	119	147	170	162
Reactor Top	70	57	90	93	104	104	110	145	164	149
		bad mixing			transient			good mixing		
Feed Rate of (dry) peat, g/h	364	517	420	483	293	477	355	427	507	0
Absolute Moisture Content of Final Product, $\left(\frac{\text{kg H}_2\text{O}}{\text{kg peat}}\right)$	0.091	0.122	0.038	0.035	0.019	0.028	0.016	Nil	Nil	—

* All experiments performed at constant flow of air of 115 litres/min at 21°C, 1 atm

$$= \left(\begin{array}{c} \text{flow through} \\ \text{the plenum chamber} \\ = 100 \text{ l/min} \end{array} \right) + \left(\begin{array}{c} \text{flow through} \\ \text{the feeding line} \\ = 15 \text{ l/min} \end{array} \right)$$

Initial moisture content of Sogevex peat taken as $0.8 \frac{\text{kg water}}{\text{kg dry peat}}$

In addition to the drying runs, one test (Run 1) was carried out with no peat feed in order to establish a heat-loss baseline for heat balance calculations. In this test, no feed entrainment gas was used, but only the 100 l/min of flow to the plenum chamber. This test also verified the agreement of plenum and bed thermocouple temperature readings in the absence of an evaporative heat sink as in drying.

The results given in Table 4.3 show that in order to have sufficiently turbulent fluidization as indicated by a uniform temperature in the reactor vessel, the incoming drying air has to be at a temperature above 240°C or the volumetric flow of this air has to be increased from 100 litres/min (21°C, 1 atm). Also, during experiment 4 the peat in the reactor caught fire, indicating that the maximum air temperature should be lower than 330°C. The potential fire hazard did not allow the electrical heating rods inserted into the bed to be used. Steady temperature profiles in the reactor were achieved quite slowly (30 to 45 minutes) and were very sensitive to feed rate fluctuations, inasmuch as the heat supply from the incoming fluidizing gas was constant.

An apparent air residence time for the experiments in Table 4.3 can be calculated as follows, for example, for an average air temperature of 100°C, Run 6,

Total flow of air = $100 + 15 = 115$ liters/min @ 21°C , 1 atm

(115) $\frac{(273 + 100)}{294} = 146$ liters/min @ 100°C , 1 atm

Reactor volume (net) 2.46 liters (see Table 3.1)

Residence time of air $\left(\frac{2.46}{146}\right) (60) = 1.0$ second

Following these preliminary trials which established suitable operating conditions, a number of steady state drying tests were carried out. All measurements and samples for these runs were taken after steady temperatures in the reactor vessel were achieved. The flowrate of the feeding line air was kept constant at the value of 15 liters/min @ 21°C , 1 atm. Moisture content of the air used was checked by a gravimetric method, by use of a silica gel adsorber followed by MS5A molecular sieve packing. The weight gain of the adsorber for a metered quantity of air was measured. A sample calculation of inlet air water content is given below.

200 liters of air increased the weight of silica gel - molecular sieve adsorbers by 0.60 grams,

therefore, moisture content of inlet air was

$$\frac{0.60 \text{ g}}{200 \text{ liters}} = \frac{0.0030 \text{ g}}{\text{liter}} = \frac{0.0030 \text{ g}}{1.202 \text{ g}} = 0.0025 \frac{\text{g H}_2\text{O}}{\text{g air}}$$

Results of these drying tests are given in Table 4.4.

Runs 11 and 12 were performed with the same temperature of drying air but the feed rate of the wet peat was different. Larger feed rate of peat of Run 11 had an obvious effect in lowering the reactor top temperature, and in giving a higher moisture content of the product peat.

Runs 13 and 14 were carried out at the drying air temperature found to be a minimum for the chosen air flow rate of 100 liters/min (see Table 4.3). This temperature of 243°C did not allow complete drying of the peat during experiment 14. The high feed rate of wet peat kept the products leaving the reactor vessel at a temperature of only 86°C.

Runs 15 and 16 were identical, and were performed to get some idea of the reproducibility of the data. For these experiments, the flowrate of the air going through the plenum chamber was increased to 125 liters/min.

Run 17 was carried out at the same conditions as Runs 15 and 16 but with a smaller feed rate of wet peat. As expected, the temperature of the exit product streams was somewhat higher than for runs previously carried out (15 and 16) at the same conditions but at higher peat feed rates.

Table 4.4

Drying Tests
Steady State Experiments

Run #	11	12	13	14	15	16	17
	Temperature, °C						
Plenum Chamber	279	277	242	242	243	243	243
Fluid Bed	115	157	125	89	116	115	137
Reactor Top	110	150	120	86	113	112	132
Feed Rate of peat, (dry basis), grams/hour	489	308	298	508	525	505	372
Absolute Moisture Content of Product ($\frac{\text{kg H}_2\text{O}}{\text{kg peat}}$)	0.022	0.004	0.013	0.044	0.026	0.017	0.009
Flowrate of Air through Plenum Chamber ($\frac{\text{liters}}{\text{min.}}$, 21°C, 1 atm)	100	100	100	100	125	125	125
App. Air Residence Time, second (water vapour not included)	1.0	1.0	1.0	1.0	0.8	0.8	0.8

Peat particles leaving the fluidized bed drier should have moisture contents close to the equilibrium value corresponding to the air temperature at the top of the reactor. Theoretically, streams leaving the fluidized bed drier at temperatures higher than 100°C should carry totally dry peat. However, this is not the case, due both to the nature of the bonding of the last 5% or so of water content, and to the heat and mass transfer dynamics of the fluidized bed used. The relation between top reactor temperature and moisture content of peat is shown in Figure 4.8. This graph indicates that the main factor accounting for the apparent non-equilibrium above 100°C must be due to the fact that the small amount of residual moisture is strongly bound to the peat. One should mention here that the oven method of moisture determination for peat samples, which leads to the peat being close to totally dry, probably contains some error due to peat hygroscopicity and to the slow decomposition of peat at 105°C.

Steady state drying tests were also carried out in the TGA apparatus using the other three peat samples as feed. A summary of the physical description of the four peat samples, the observed drying rates in the constant rate period and the cellulose contents are given in Table 4.5. The critical moisture content appears to be a function of both the degree of degradation of the peat, and of the fibre

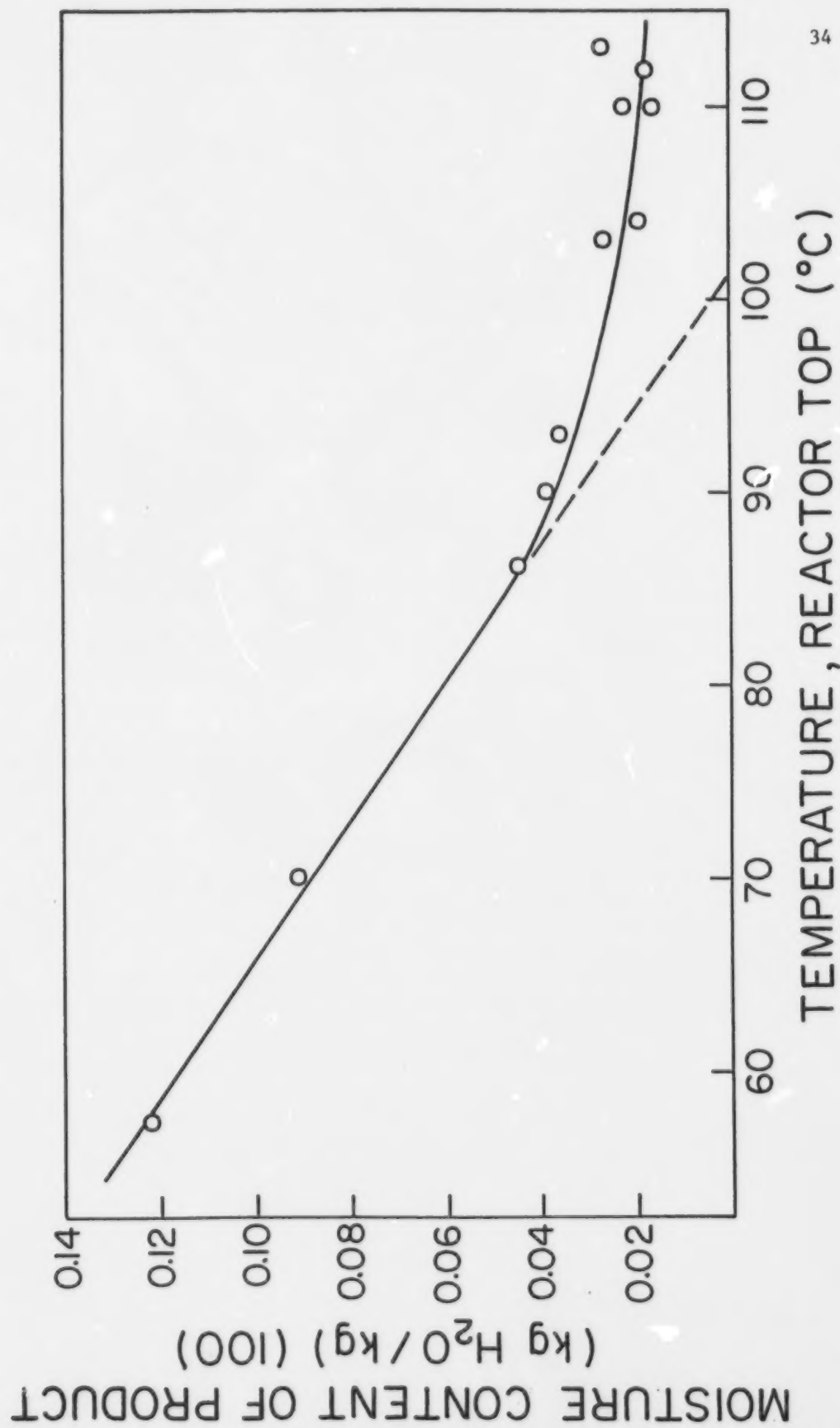


Figure 4.8 Fluidized Bed Drying of Sogevex Peat - Effect of
Reactor Temperature on Final Product Moisture
Initial Moisture, 0.8 kg/kg

Table 4.5

Summary of Some Properties of Peat Samples
High Moor Peats

Name	Source	Description	Level of Degradation	Length of Fiber
1. Premier Peat	Rivière-du-Loup	black peat, bottom	high	short
2. Namsco	Rivière-du-Loup	brown peat, middle	medium	short
3. Pit Moose	Pointe-au-Père	blond (yellow), top	low	short
4. Sogevex	Baie-Comeau	blond (yellow), top	low	long

	Critical Moisture [kg water/kg B.D. Peat] x 100	Drying Rate in Constant Rate Period [kg/kg min]	Initial Water Content [kg water/kg B.D. Peat]	Cellulose* Content
1.	37 ± 5	1.0	1.2	23.3
2.	13.5 ± 2.5	0.6	0.55	23.1
3.	12.5 ± 2.5	0.5	0.4	21.4
4.	15 ± 2.5	0.8	0.7	23.2

* Nitric acid - acetic acid digestion method.

length, although the former is more important. The constant drying rate also decreased for younger and shorter fibre peats. The age of the peat did not appear to have any significant effect on the cellulose contents of the four peat samples used in this work.

The constant drying rate, which accounts for the bulk of the water removal, is given by the relation

$$W_0 - W = K\Theta$$

where W_0 = initial moisture content, kg/kg dry peat

Θ = drying time in minutes

K = constant rate, kg water/(kg peat)(min).

The magnitude of the constant rate of drying which can be achieved depends on the temperature of the fluidized bed. The particle itself will approach the adiabatic saturation temperature in the constant rate period, and will not exceed this temperature until the moisture content reaches a low value and the falling rate period begins. Therefore, if peat is not dried below about 10% moisture, the structural changes that occur in younger peats due to overheating may not take place.

4.1.3 Heat Balances

Data from Runs 11 to 17 are sufficiently accurate at steady state so that they can be used for engineering calculation of heat and mass balances around a fluidized bed drier, for

mathematical modelling, process simulation, etc. To perform heat balances one needs two additional parameters:

1. heat losses;
2. heat capacity of peat.

Perry's Chemical Engineering Handbook gives the following values:

Heat Capacity (cal/g C)	coals	woods
	0.26 to 0.37	0.45 to 0.65

It is probably safe to assume that the heat capacity of peats would be in the range of 0.37 to 0.45 cal/g C.

Heat losses can be estimated from the data of Run 1, and a calculation gives a value of 0.046 cal/s per °K of temperature differential.

Data from Table 4.3 for the preliminary experiments generally show about 15% more heat output than input, indicating a lack of steady state operation. The steady state results given in Table 4.4 give satisfactory heat balances, that is, within ±5%, indicating the good quality of the data.

With a datum temperature of 21°C, the heat balance can be written:

Heat entering in the fluidizing gas - heat out of the reactor as

Σ [heat loss + heat in dry air + latent and sensible heat in water vapour + heat in the exit peat product].

For example, the ratio of heat in/heat out = 0.978 for Run 12
heat in/heat out = 1.044 for Run 16.

A detailed calculation of a heat balance is given in the Appendix.

4.2 Pyrolysis of Peat in a Fluidized Bed

4.2.1 Preliminary Tests

Detailed investigations of the effect of process conditions on yields from the fast pyrolysis of peat were carried out using the Sogevex peat as the standard feed. This material was a long fibre younger yellow peat, but was somewhat more homogeneous and therefore judged to be a better test material than the older black peats.

The screen analysis of this peat as it was used for feed to the pilot plant unit was given in Table 3.3. All of this material was used as feed - no oversize or undersize was removed.

The elemental analysis of the Sogevex peat was performed in our laboratory, with results shown in Table 4.6. A comparison of these results with other peat samples investigated in our previous studies is given in Table 4.7.

Table 4.6Elemental Analysis of Sogevex Peat

Perkin-Elmer 240°C Elemental Analyzer

Sample No.	wt % mf (oven-dried samples)				wt % maf
	I	II	III	Average	
Carbon	49.23	48.11	51.20	49.5	51.40
Hydrogen	5.30	5.33	5.64	5.4	5.61
Nitrogen	1.28	N.D.	1.35	1.3	1.35
Sulphur	} by diff.				41.64
Oxygen					
Ash*	3.7	3.7	3.7	3.7	0
					100.0

* Macroscale determination

Table 4.7Comparison of Elemental Analyses of Different Peats

(Waterloo results)

Type	Negril (Jamaica)	IEA (Finland)	Sogevex (Quebec)
Carbon, wt % maf	62.0	57.14	51.40
Hydrogen	4.4	5.31	5.61
Nitrogen	3.8	1.87	1.35
Sulphur	1.8	0.24	41.64
Oxygen, by diff.	28.0	35.44	
	100.0	100.0	100.0
Ash, wt % mf	9.0	4.67	3.7
Cellulose content, wt % maf	12.9	?	24.1

The generally higher grade of the Sogevex peat is apparent (that is, it is closer in elemental composition to biomass). The Jamaican Negril peat is an earthy black/grey low moor peat, fairly highly decomposed. The IEA peat from Finland is a brown short fibred fuel grade peat. The Quebec Sogevex peat is a long fibred young peat suitable for some horticultural uses, and has an elemental composition not too different from wood or grasses, except for the much lower cellulose content and the higher nitrogen content, both reflecting the formation of humic acids.

Two initial pilot plant runs were completed (Runs 88 and 89) using the Sogevex long fibre yellow peat as feed. The basic conditions for the pilot plant fluidized bed reactor were given in Table 3.1. A gas residence time a little shorter than usual was used (0.37 or 0.35 seconds). At 554°C, a yield of organic liquids of 51.4% was obtained, while at 652°C this yield decreased to 43.3% with a large increase in gas production from 16.7% to 30.8%. Material balances were good for both runs.

Char production was about 23% to 26%, which is reasonable for a low cellulose content material such as peat. The major gases produced at both temperatures were CO and CO₂, reflecting the presence of carbonyl and carboxylic acid groups in the peat. A detailed pilot plant log sheet for Run 88 is given in the Appendix.

During these first two experiments (pilot plant Runs 88 and 89) about 50 wt % of the total organic liquid was collected in the cotton wool filter. This part of the condensed product was unrecoverable for eventual Karl-Fischer water determination of HPLC analysis.

It was assumed that the tar collected by the cotton filter had water content equal to zero, an assumption which could lead to an overstated yield of organics and a low yield of pyrolytic water.

To improve the collection system and correct the situation described above, two Schrader Bellows in-line filters with glass catch pots were added to the recovery system.

During subsequent pyrolysis runs only about 5 wt % of the "tar" was captured by the cotton wool filter. Accordingly, established procedures allowed the collection of the following liquid fractions for a given pyrolytic test:

1. Liquor - collected in the catch bottles at the bottom of the two main condensers, contained 65 to 85 wt % water/by Karl-Fischer titration;
2. Schrader Bellows catch - very inhomogeneous fraction, water content 15 to 30 wt % which was possible to determine only after adding the solvent;

3. THF-methanol washings - water content 10 to 20 wt % evaluated in the solvent phase before evaporation of solvent;
4. Cotton wool filter catch - nonrecoverable part, about 5 wt % of total tar; for material balance purposes it was assumed water content of this fraction equal to that of fraction No. 3.

This latter assumption allowed for some corrections in yields of organics and water for Runs 88 and 89 and these corrections are included in tabulated results. However, in subsequent runs, this correction caused little error due to the small amount of tar caught in the cotton wool filter.

In summary, to obtain reasonable pyrolytic water-organics yields five or six Karl-Fischer water determinations had to be performed. The yields of chars and gases did not present similar difficulties and were evaluated routinely with little error. Care was taken to ensure a uniform moisture content of the batches of peat used for each experiment. After each test a portion of the peat remaining in the feeder was taken for water determination. Values varied in the range of 10 to 27 wt %.

The twin-screw volumetric feeder delivered a high feed rate of peat with drier samples, indicating the phenomenon of shrinking of bulk volume on drying. The higher feed rate and the additional flow resistance from the newly installed

Schrader Bellows limited the run time of some tests to 50 minutes due to limitations in the capacity of the recirculating compressor.

4.2.2 Fast Pyrolysis of Peat in a Fluidized Bed

In all, twelve pilot plant runs were carried out using the Sogevex peat feed. The reactor conditions have been given in Table 3.1. The major process parameters investigated were temperature, moisture content and feed rate. The ranges of the experimental parameters covered by these tests are given below:

<u>Parameter</u>	<u>Range</u>
Temperature, °C	460 - 692
App. Residence Time, sec	0.35 - 0.49
Moisture, wt %	6.5 - 30.9
Feed Rate, kg/h	0.86 - 2.01

A tabulation of the results of pyrolysis tests for all runs is given in Table 4.8. The runs are arranged in order of increasing temperature in order to show the effects of this major variable. Interestingly, temperature does not affect the yield of organics to any degree in the temperature range of 460° to 555°C, with 44% to 49% yield mf being obtained. The yield of organics is a little higher in the 500° to 550°C range. However, later results will show that the

Table 4.8
Summary of Pilot Plant Tests, Sogevex Peat

Pilot Plant Run #	105	103	95	101	94	106	96	102	88	97	89	104
Sogevex Peat Run #	11	9	4	7	3	12	5	8	1	6	2	10
Temperature, °C	461	460	475	505	506	511	528	550	554	596	652	692
App. Residence Time, sec	0.49	0.46	0.43	0.45	0.44	0.49	0.43	0.43	0.37	0.44	0.35	0.38
Feed Rate, kg/hr	1.27	1.84	1.80	1.57	1.09	1.62	2.01	1.79	0.86	1.97	1.18	1.00
Amount Fed, grams	2420	2572	2223	2538	2333	5614	1873	1343	1627	1678	2365	1829
Moisture, wt %	30.9	7.0	16.9	10.3	27.1	21.9	10.2	6.5	25.4	16.1	25.4	7.8
Yields, wt %, mf												
Gas	12.85*	11.25*	10.86	14.26	12.8*	15.34*	16.0	16.83	16.7	22.9	30.9	36.86
Char	34.45	35.15	34.31	30.75	32.54	30.34	28.34	25.49	26.08	25.97	23.04*	25.94
Water	8.22	8.50	9.26	9.80	6.98	10.1	9.36	9.3	7.90	6.51	7.23	11.50
Organics	44.43	45.11	45.34	47.80	47.67	44.23	45.88	46.13	48.94	40.89	38.90	25.31
Total	100.0	100.0	99.8	102.6	100.0	100.0	99.6	97.75	99.6	96.9	100.0	99.61
H ₂	0.02	0.01	0.01	0.02	0.01	0.02	0.02	0.03	0.02	0.01	0.13	0.19
CO	3.58	2.29	2.55	3.86	3.92	4.20	4.57	5.52	5.16	9.41	14.80	20.10
CO ₂	8.37	8.29	7.62	9.18	7.96	10.03	10.05	9.51	9.86	10.32	10.50	9.58
CH ₄	0.46	0.17	0.26	0.52	0.57	0.46	0.50	0.60	0.56	1.32	2.18	2.78
C ₂ H ₆	0.20	0.06	0.09	0.16	0.10	0.17	0.21	0.22	0.31	0.56	1.13	1.60
C ₂ H ₄	0.05	0.02	0.03	0.07	-	0.07	0.07	0.10	0.08	0.17	0.36	0.57
C ₃ H ₈	0.05	0.04	0.04	0.08	-	0.09	0.10	0.14	0.13	0.19	0.32	0.52
C ₃ +	0.12	0.36	0.27	0.37	0.23	0.31	0.48	0.71	0.61	0.94	1.42	1.52

* Corrected (due to some leaks in compressor, feeder assembly) to 100% of total balance

character of the organics produced is affected significantly by temperatures in this range. Above 550°C the tar yield decreases rapidly with a corresponding increase in gas yield. It is also interesting that from 460° to 500°C, char yield is decreased and gas yield increased, possibly indicating some incompletely decomposed peat at the lowest temperatures. CO and CO₂ are the major gaseous products at all temperatures, but above 600°C the yield of hydrocarbon gases increases and at 692°C the yield of hydrocarbon gases reaches 7.0% of the mf feed.

A comparison of Runs 11 and 9 at 460°C, Runs 7 and 3 at 505°C and Runs 102 and 88 at 550°C shows that variation in feed moisture content from 6.5% to 30.9% had very little effect on product yields, particularly yields of condensable organics, or on gas compositions, indicating that the additional water vapour was an inert component even at 550°C. Similarly, there appears to be little effect of moisture content on liquid composition.

High moisture content of the feed generally led to lower feed rates because of the greater bulk of the feed. However, these changes in feed rate, from 0.86 kg/h to 1.84 kg/h, did not appear to cause any significant changes in product yields, indicating that within this range, the pyrolysis process was not limited by heat transfer processes.

Vapour residence time was not varied significantly in any of these tests. Runs 102 and 88 at 550°C were carried out at 0.43 and 0.37 seconds residence time, respectively. While Run 88 with the shorter residence time had a slightly larger liquid product yield, as expected, this could also be accounted for by a better material balance for Run 88. No conclusions concerning the effect of residence time can be drawn from the results in Tables 4.6 or 4.8.

For some preliminary "tar" evaluation tests, the presently used routine method developed for analysis of liquid products of cellulose pyrolysis was adopted. Details of the analysis are given in Table 4.9. This technique is limited to water-soluble components, and allows the determination of acids, alcohols, sugars and some bifunctional ketones and aldehydes.

The Sogevex peat contains ≈ 20 wt % of cellulose which gives thermal decomposition products fitting the definition above. Of the four "tarry" fractions collected for each test, the best suited for this HPLC analysis were the liquors (fraction 1). In a similar way, soluble parts of fraction 3 were analyzed. To arrive at some general indications it was assumed that the organic water-soluble parts of fractions 2, 3 and 4 were similar to each other. This is an approximation which may lead to some errors, but fractions 2, 3 and 4

Table 4.9

Data for HPLC - analysis

Column: Aminex HPX-87H, 300 x 7.8 mm obtained from Bio-Rad Laboratories
(Canada) Ltd., Mississauga, Ontario L4X 2C8

Eluent: 0.07 N H_3PO_4 , isocratic

Flow rate: 0.32 x 2.5 ml/min

Temp.: 65°C

Internal standard: propanol - 1

Detector: R.I. refractometer, R 401 - Waters

only represent 15% to 35% of the total tar yield, so any error is minimized. The results of the combined yields of water-soluble organics from the four tar fractions are given in Table 4.10. Also shown in this table are the results of analysis of the aqueous fractions of the tar, giving the amounts of organics found in each phase.

The results presented in Tables 4.8 and 4.10 are also shown in Figures 4.9 to 4.14.

Figures 4.9 and 4.10 show the product yields on a moisture free basis. Maximum yield of organic liquids was obtained in the range of 475° to 550°C, and Figure 4.9 shows a rather broad, flat optimum region. Char yield shown in Figure 4.10 decreases with temperature up to 600°C and then becomes constant. Gas yield increases steadily with temperature, suggesting that above 600°C tar yield is lost by cracking to gaseous components, and not by degradation to char.

Figure 4.11 shows one of the most interesting results of this study, the rapid change in the fraction of tar which is water soluble over the region of maximum liquid yield. At 475°C, with a 47% tar yield, about 68% of this tar is water soluble. At 550°C, where the tar yield is also 47%, only about 45% of this is water soluble. At 600°C, with a tar yield of 42%, the water soluble fraction is 38% of the tar.

Table 4.10
Analysis of Water Soluble Components of Pyrolysis Tar

Pilot Plant Run #	105	103	95	101	94	106	96	102	88	97	89	104
Sogevex Peat Run #	11	9	4	7	3	12	5	8	1	6	2	10
Temperature, °C	461	460	475	505	506	511	528	550	554	596	552	592
Yields, wt %, mf												
Total Organic Liquid	44.43	45.11	45.34	47.80	47.67	44.23	45.88	46.13	48.94	40.9	38.9	25.31
Water Insoluble	14.0	13.4	14.6	13.6	16.0	15.4	24.4	25.8	31.4	21.3	30.6	13.8
Water Soluble	30.4	31.7	30.7	34.2	31.7	28.8	21.5	20.3	17.5	19.6	8.3	11.5
Water Soluble Component's												
1. Oligosaccharides	0.12	0.17	0.29	0.09	0.22	0.13	0.24	0.09	0.17	0.15	0.09	0.03
2. Cellobiosan	1.64	1.58	1.24	0.99	1.03	1.08	0.74	0.92	0.64	0.70	0.15	-
3. Glucose	0.66	0.76	0.50	0.39	0.53	0.43	0.31	0.33	0.38	0.29	-	-
4. Fructose	2.58	2.50	1.33	1.82	1.45	1.21	1.18	1.31	0.94	0.75	0.26	0.04
5. Glyoxal	0.24	0.13	0.65	0.14	0.14	0.24	0.17	0.14	0.65	0.79	0.33	0.17
6. Glycerinaldehyde	1.89	2.25	1.58	1.64	1.70	1.38	1.05	1.27	0.74	1.07	0.25	0.38
7. Methylglyoxal	8.29	8.75	5.72	7.53	7.60	6.18	5.05	6.13	5.45	5.34	2.03	1.94
8. Levoglucosan	0.86	0.79	1.52	0.80	0.67	0.82	0.61	0.77	1.04	1.51	1.87	1.03
9. Hydroxyacetaldehyde	1.63	-	0.23	-	1.45	0.55	-	-	0.38	-	0.53	-
10. Formic Acid	0.36	-	0.24	-	0.26	0.27	0.30	0.23	0.42	0.31	0.62	0.50
11. Formaldehyde	0.96	1.70	1.86	0.44	1.67	1.09	0.79	0.77	0.73	1.23	0.89	0.90
12. Acetic Acid	-	-	-	-	-	-	-	-	-	-	-	-
13. Ethylene Glycol	0.18	0.30	0.57	0.34	0.46	0.32	0.29	0.37	0.26	0.42	0.51	0.44
14. Acetol	-	-	0.33	0.75	0.14	-	-	-	-	0.28	-	0.20
15. Methanol	-	-	-	-	-	-	-	-	-	-	-	-
Total Above	19.4	18.9	16.1	14.9	17.3	13.7	10.7	12.33	11.8	12.8	7.5	5.6

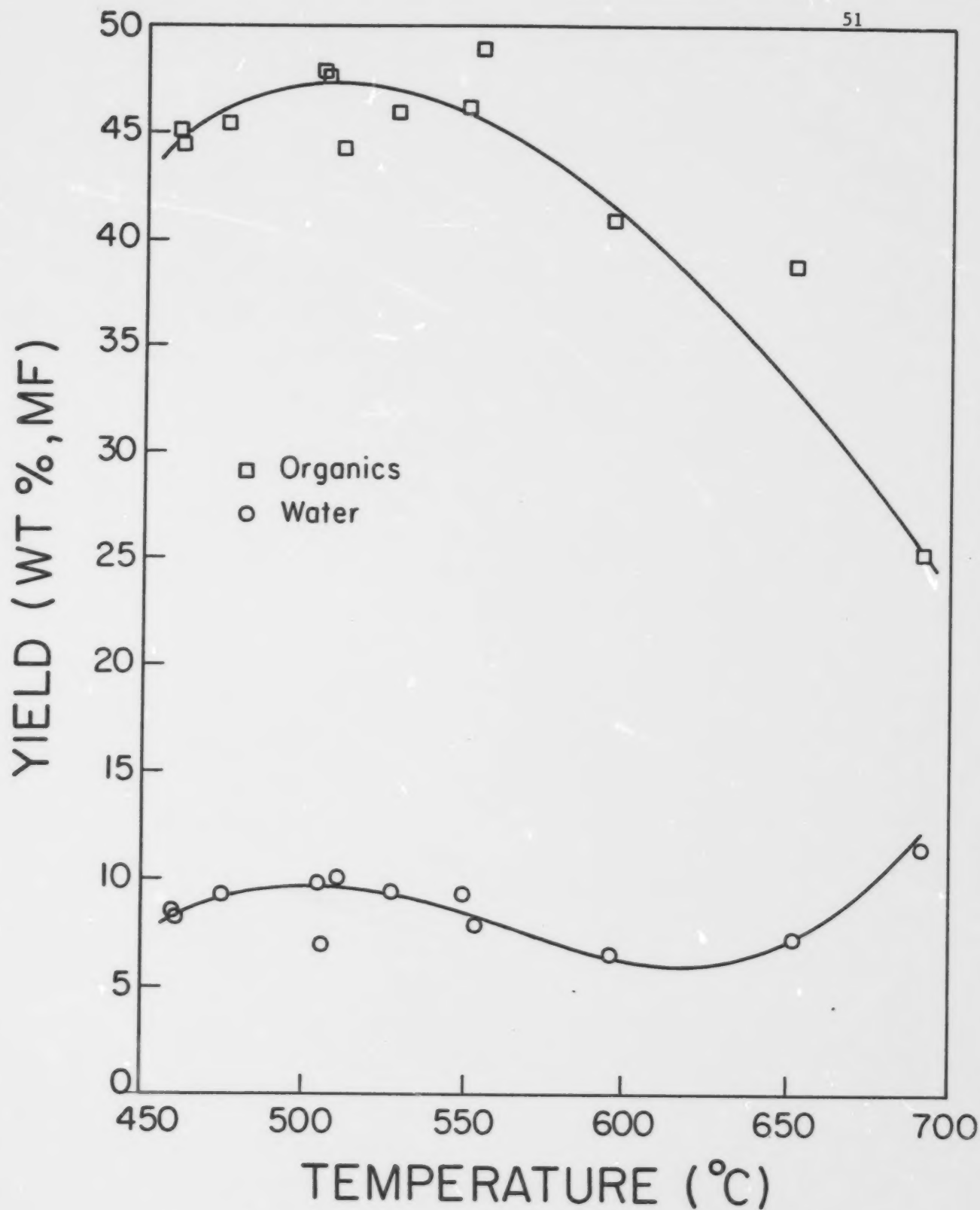


Figure 4.9 Pyrolysis of Sogevex Peat - Effect of Temperature on Yields of Organic Liquids and Product Water

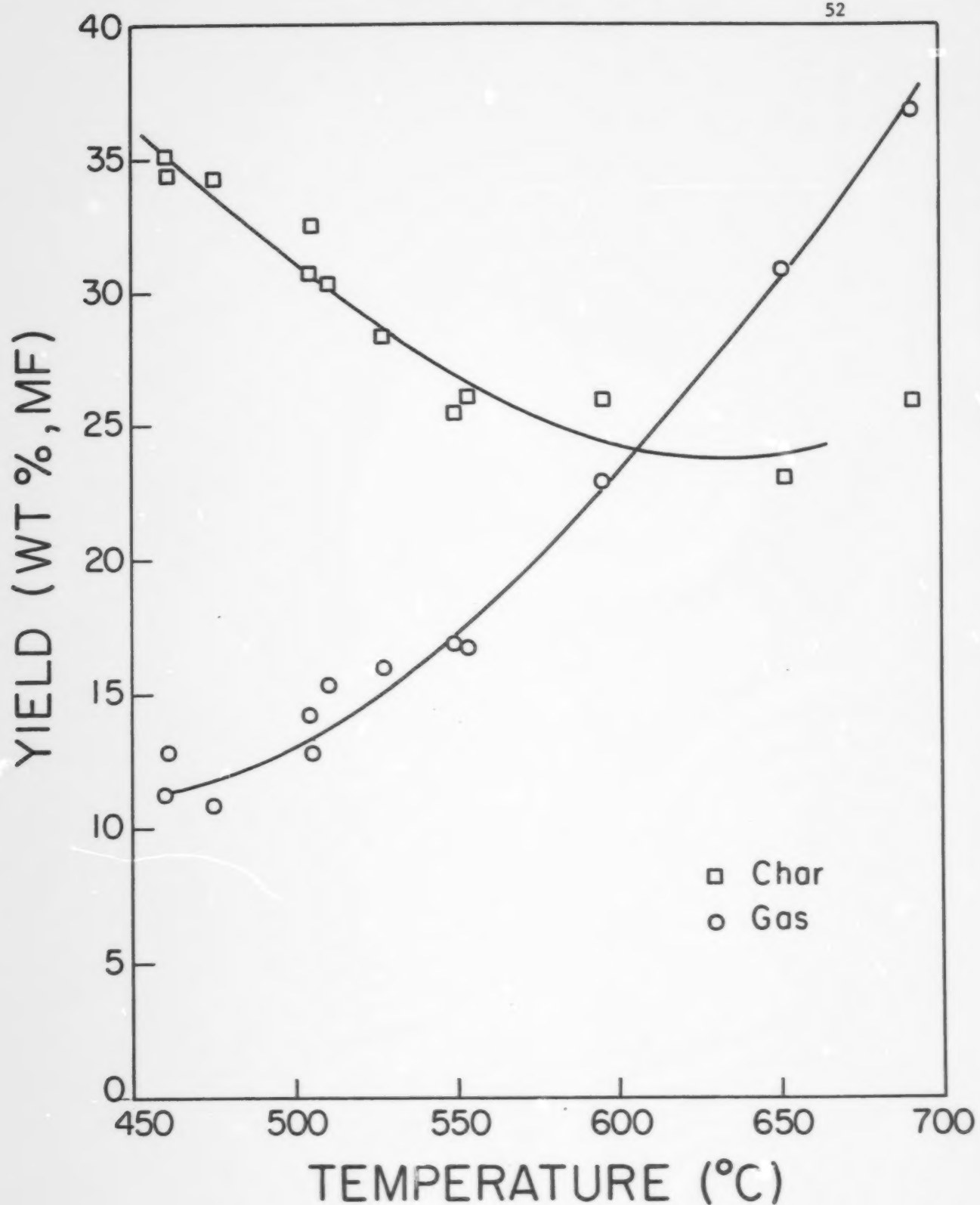


Figure 4.10 Pyrolysis of Sogevex Peat - Effect of Temperature on Yields of Gas and Char

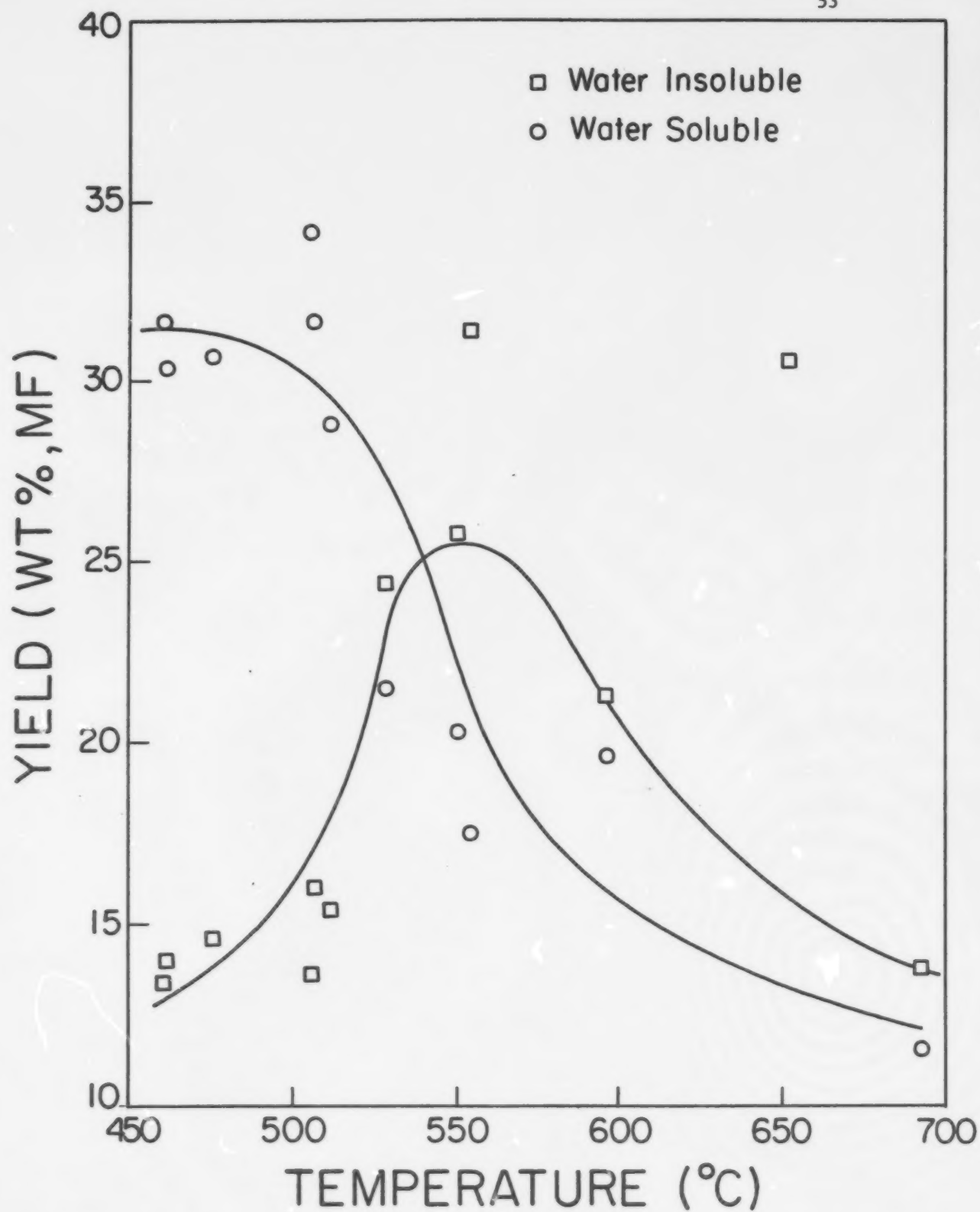


Figure 4.11 Pyrolysis of Sogevex Peat - Yields of Water Solubles and Water Insolubles in Liquid with Temperature Change

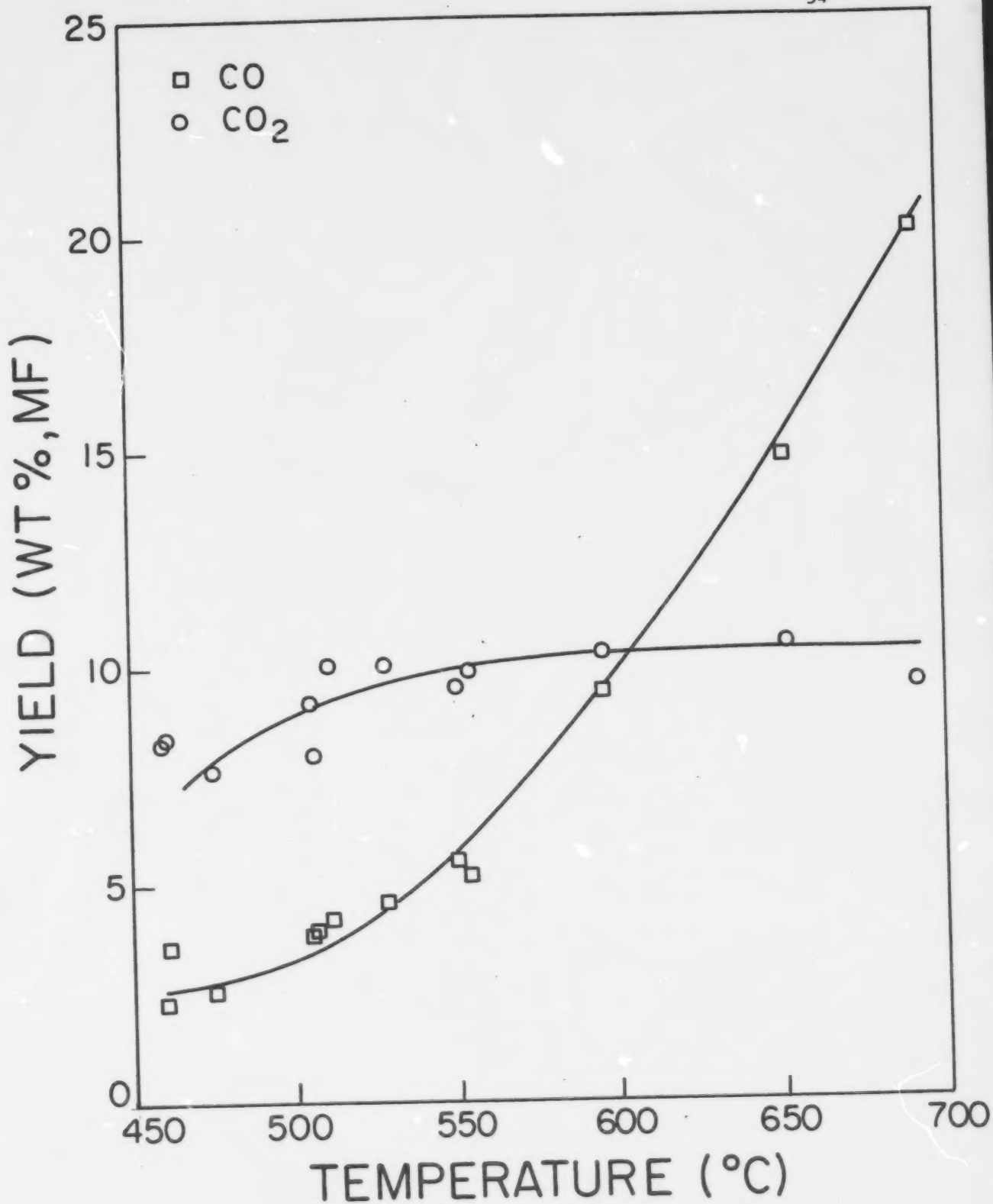


Figure 4.12 Pyrolysis of Sogevex Peat - Change in CO and CO₂ Yields with Temperature

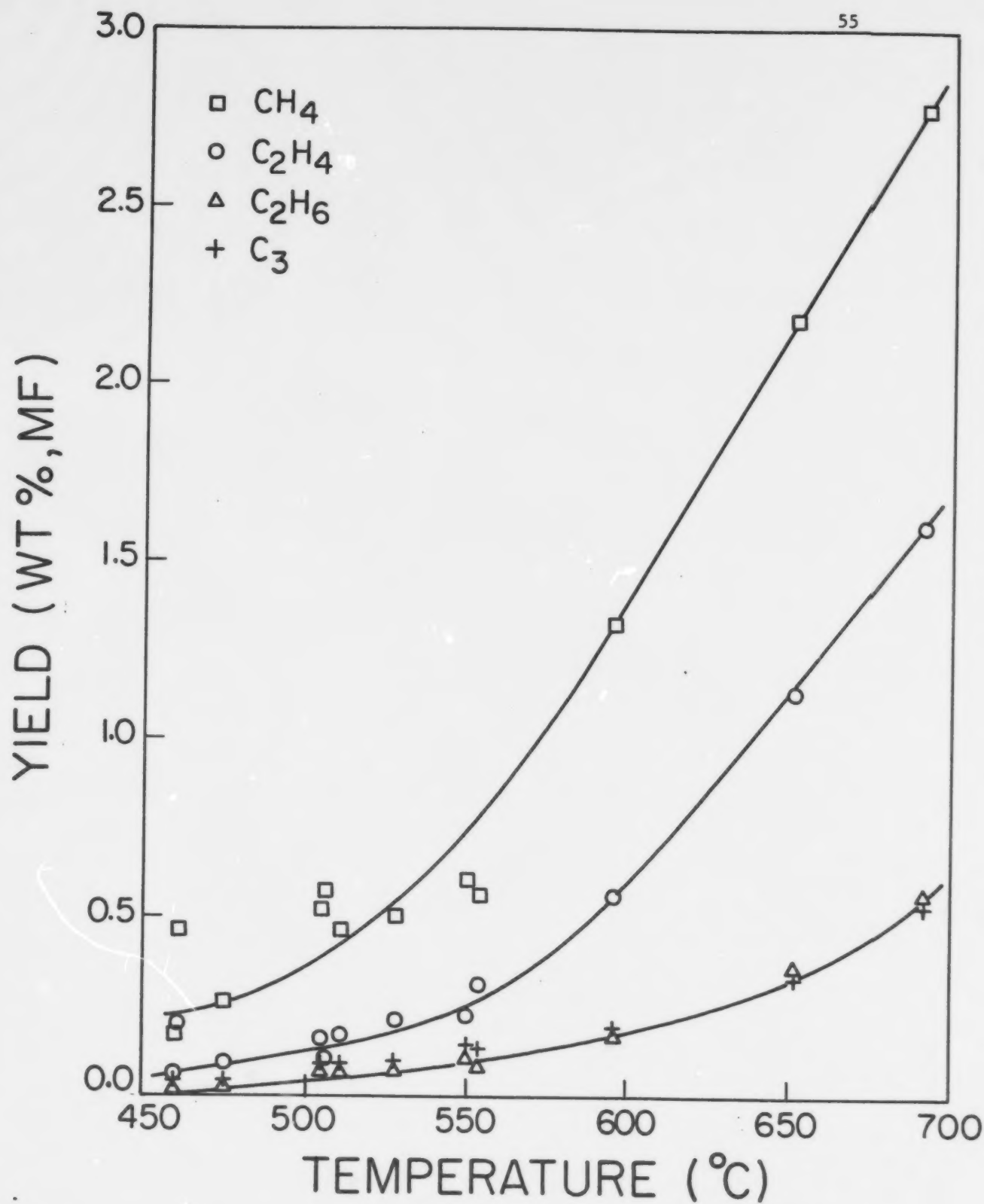


Figure 4.13 Pyrolysis of Sogevex Peat - Change in Hydrocarbon Gas Yields with Temperature

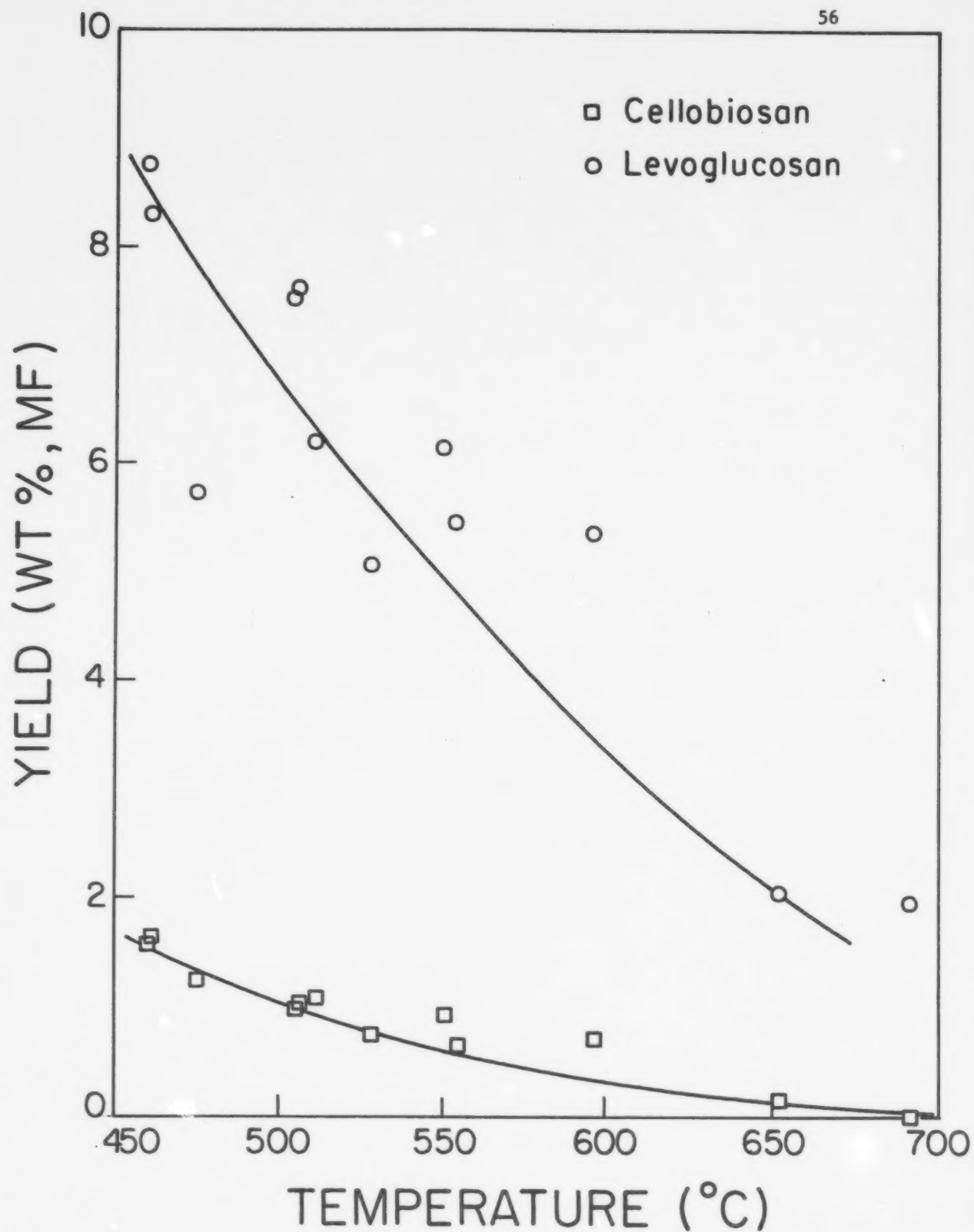


Figure 4.14 Pyrolysis of Sogevex Peat - Change in Liquid Composition with Temperature

Figure 4.12 shows the yields of CO and CO₂, which exhibit trends typical of fast biomass pyrolysis. Hence, the loss of water solubility, especially at higher temperatures, is not due entirely to decarboxylation. Figure 4.13 shows the yield of light hydrocarbon gases, which are all about 0.5% or less in the optimum range of temperatures.

The yields of two of the principal individual components formed from the cellulose fraction of the peat, levoglucosan and cellobiosan, are shown in Figure 4.14. In comparison with results from a 100% cellulose (Avicel), these yields do not display a maximum value around the optimal temperatures for liquid yield, but show a steady decrease with temperature, consistent with the decrease in the yield of water soluble material in the tar.

Two photographs as Figures 4.15 and 4.16 are attached showing the peat feed (Sogevex) and the char product from the peat. The grid is 1 mm x 1 mm. The char retains much of the shape and size of the original feed particles, a characteristic of the Waterloo Fast Pyrolysis Process for wood particles as well.

4.2.3 Elemental Analyses of Pyrolysis Products from Peat

The elemental analyses of the char and tar products produced from Sogevex peat for all runs are summarized in Table 4.11. Runs are arranged in order of increasing temperature. Yield

Figure 4.15
Peat Feed (Sogevex)

58



Figure 4.16
Char Product from the Peat

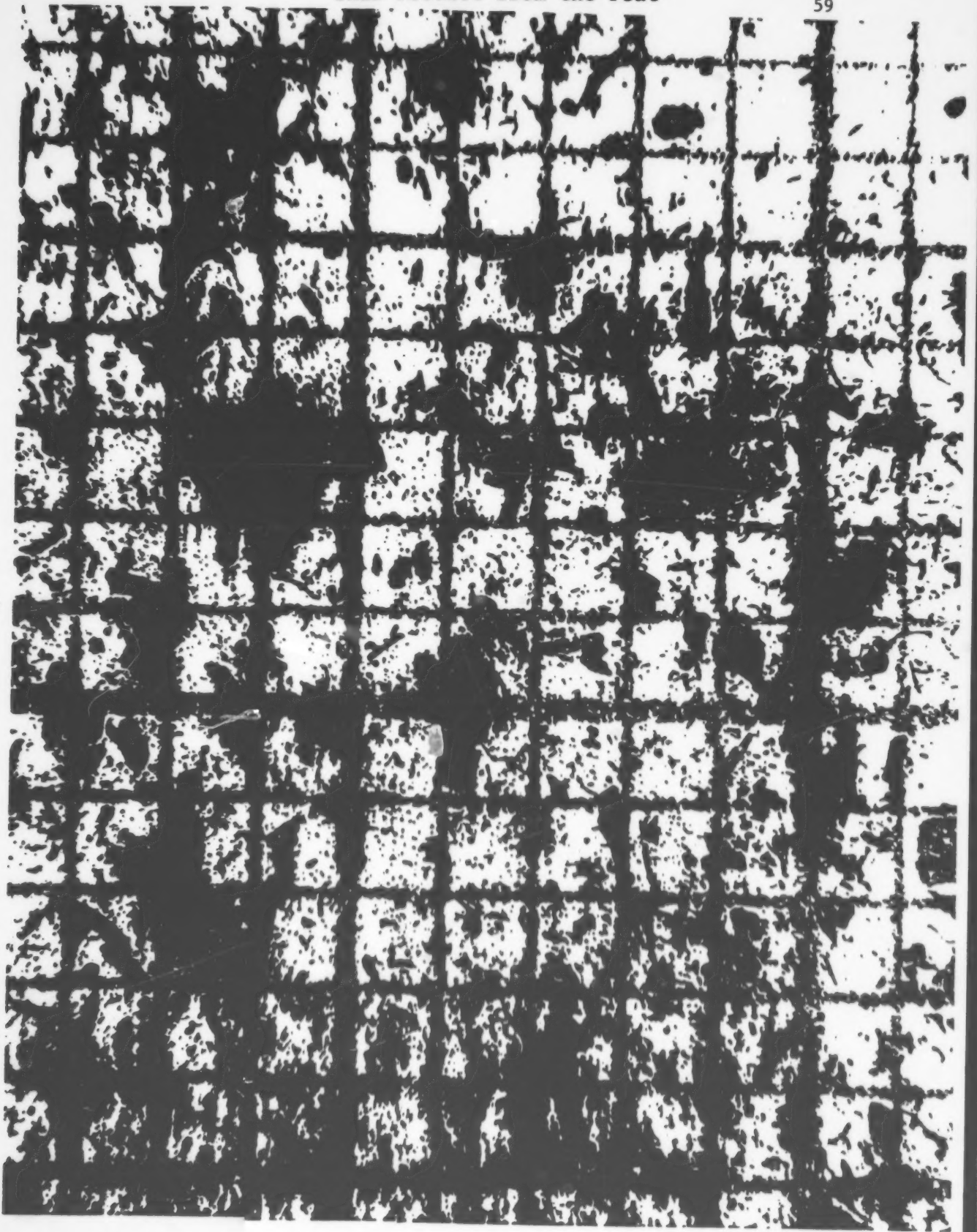


Table 4.11

Results of Elemental Analyses - Sogevex Peat

Pilot Plant Run No.	105	103	95	101	94	106	96	102	88	97	89	104
Temperature °C	461	460	475	505	506	511	528	550	554	596	652	692

Weight %

CHARS

Carbon	63.01	63.69	64.99	64.86	67.05	65.37	66.40	63.15	63.77	70.00	67.23	74.51
Hydrogen	3.49	3.65	2.86	3.12	2.30	2.94	1.97	2.90	2.16	2.49	1.98	2.78
Nitrogen	1.07	1.05	0.77	1.62	0.78	1.05	0.11	0.83	0.30	1.08	0.69	0.94

TARS (moisture free)

Carbon	54.01	52.30	55.25	56.02	56.78	48.06	55.78	55.78	56.62	56.61	59.69	63.62
Hydrogen	6.86	6.55	6.99	7.23	6.96	7.42	6.90	6.65	8.46	6.99	7.57	7.30
Nitrogen	0.67	0.75	0.86	0.63	0.80	1.96	1.35	1.65	1.20	2.18	2.25	2.53
H/C	1.52	1.50	1.50	1.55	1.47	1.85	1.48	1.43	1.79	1.48	1.52	1.38

data and operating conditions for all runs were given in the previous tables. As expected, the C content of chars increases with temperature while the H content decreases. Nitrogen content, which is higher in peats than in other biomass, appears not to vary with temperature in the chars. The tar shows that both C and H increase somewhat as temperature increases, with the result that the H/C ratio is reasonably constant at about 1.5. The occasionally erratic results for the tar C/H/N analyses reflects mainly the difficulty in micro sampling the tar, which is not a homogeneous liquid.

Trial carbon and hydrogen balances for Runs 88 and 89 are given in Table 4.12. In general, the closure of the balances is satisfactory, given the sampling difficulties mentioned above, and verifies the procedures used and the validity of the assumptions made.

4.2.4 Characterization of Liquid Pyrolysis Products from Peat

Two runs, 101 and 102, were selected for further analysis of the tar fractions because they span the temperature range of 500° to 550°C in which the nature of the liquid product appears to show the greatest change, as reflected in the change in amounts of water-soluble components. Equipment used and conditions for the analysis of the sample from Run 101 are listed below.

Table 4.12

Typical C and H Balances - Sogevex Peat Pyrolysis Products

Peat Analysis

Carbon	wt % mf	49.5
Hydrogen	"	5.4

		<u>PP 88</u>	<u>PP 89</u>
Char			
	Hydrogen wt %	2.16	1.98
	Carbon "	63.77	67.23
Tar			
	Hydrogen	8.46	7.57
	Carbon	56.62	59.69

Balances

Yield, wt % mf				Yield, wt % mf			
		<u>Carbon</u>	<u>Hydrogen</u>		<u>Carbon</u>	<u>Hydrogen</u>	
Char	26.08	16.63	0.56	23.04	15.49	0.46	
Tar	48.94	27.71	4.14	38.90	23.22	2.94	
Water	7.90	-	0.88	7.23	-	0.80	
H ₂	0.02	-	0.02	0.13	-	0.13	
CO	5.16	2.21	-	14.80	6.34	-	
CO ₂	9.86	2.69	-	10.50	2.86	-	
CH ₄	0.56	0.42	0.08	2.18	1.64	0.54	
C ₂ H ₄	0.31	0.27	0.04	1.13	0.97	0.16	
C ₂ H ₆	0.08	0.06	0.02	0.36	0.29	0.07	
C ₃	0.13	0.11	0.02	0.32	0.27	0.05	
C ₄	0.61	0.52	0.09	1.42	1.22	0.20	
		50.62	5.85		52.30	5.35	
		102.27%	108.33%		105.7%	99.1%	

GC-MS Equipment:

H-P 5890 Gas Chromatograph

H-P 5970 Mass Selective Detector

H-P Crosslinked methyl-silicone column

Selected Parameters of GC-MS Analysis:

Scanning Range	20 to 300 amu
Initial Temperature	60°C
Initial Time	2 min
Ramp Rate	10 deg/min
Final Temperature	240°C
Injection Port Temp.	250°C
Transfer Line Temp.	250°C.

Figures 4.17 to 4.20 show the results of the GC-MS analysis of a liquor sample (fraction 1) from Run 101. Some preliminary assignments of peaks are listed in Table 4.13. Most of the readily identified compounds are water soluble to some extent.

Samples of the whole tar from Run 102 at 550°C and of the water-soluble and water-insoluble fraction of the tar were analyzed by GC-MS. Analytical conditions are given in Table 4.14 and spectra are shown in Figure 4.21. A sample of this tar was fractionated also by successive hexane and then toluene extraction, and samples of the hexane and toluene

Figure 4.17

64

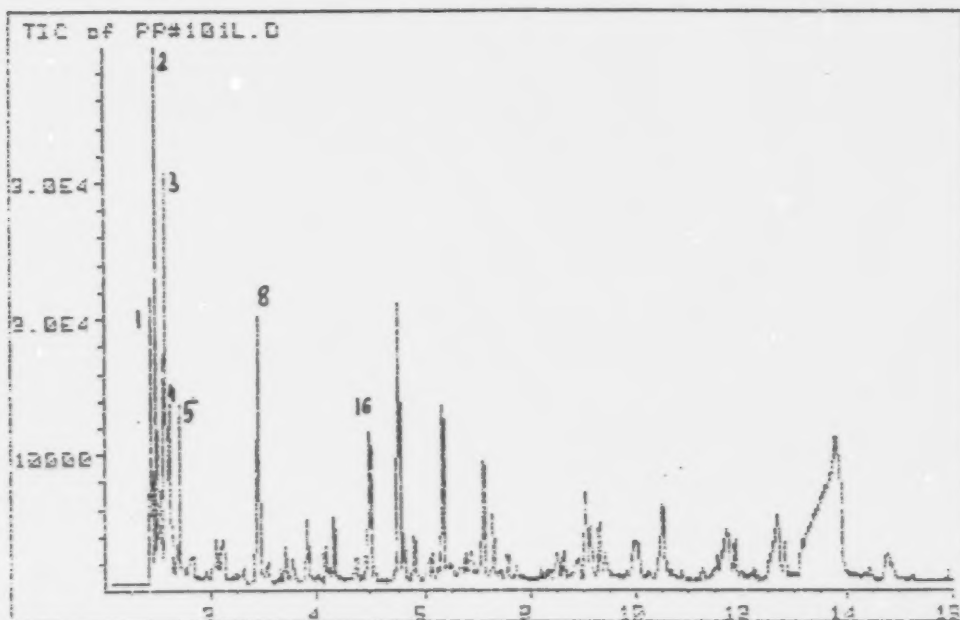
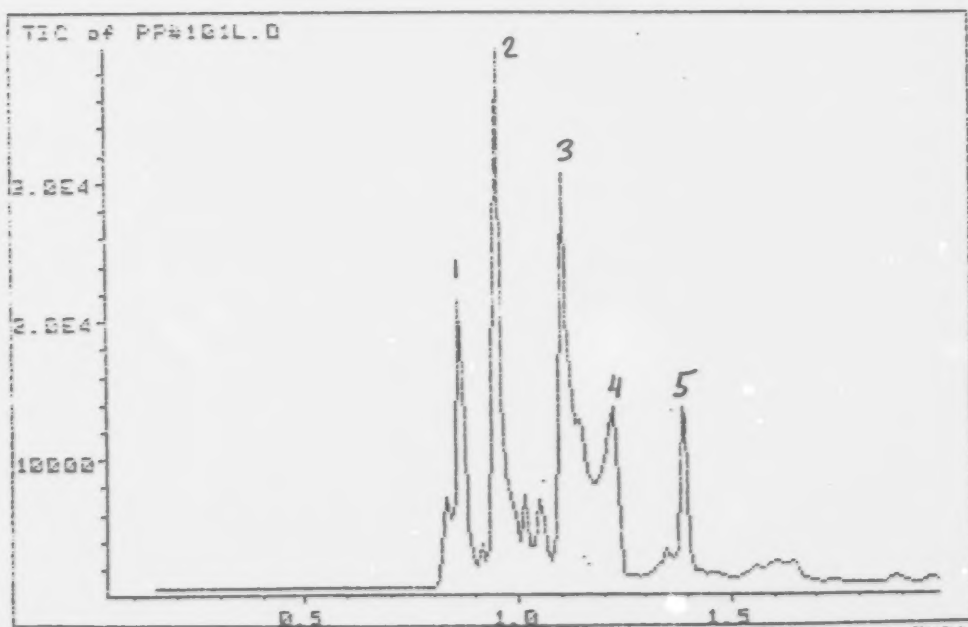


Figure 4.18



GC/MS of Peat Pyrolysis Oil, Run 101

Figure 4.19

65

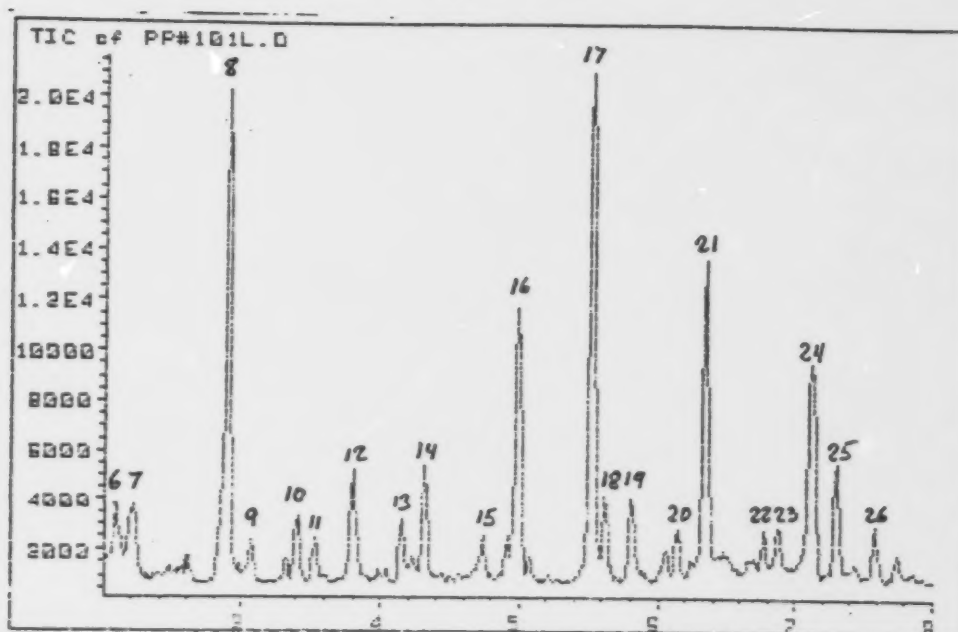
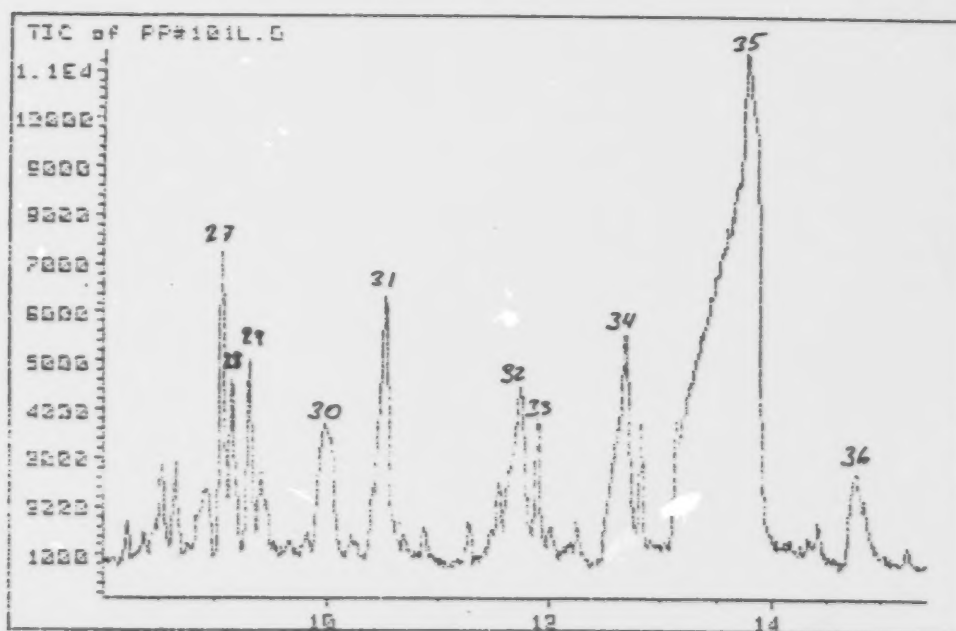


Figure 4.20



GC/MS of Peat Pyrolysis Oil, Run 101

Table 4.13

Preliminary Assignments of Peaks

Peak No.	Identification (90% or better match quality with NBS-Mass Spectral Database)
2	Pyruvaldehyde
3	Hydroxyacetaldehyde
4	Acetic Acid
5	Acetol
6	2-Hexanon, 4-hydroxy-3-propyl
7	Acetic acid, ethenyl ester
8	2-Furancarboxaldehyde (furfural)
9	2-Pentanone, 3-methyl
16	2-Furancarboxaldehyde, 5-methyl (methyl furfural)
28	1-2-Benzenediol

Table 4.14

Procedures for Analysis of Liquid Product of Run 102

Parameters of GC-MS - Selected for Tar #102 Analysis:

Scan Range	20 - 450 amu
Initial Temperature	60°C
Initial Time	2 min
Ramp Rate	10 degree/min
Final Temperature	300°C
Injection Port Temp.	300°C
Transfer Line	300°C
Solvent Delay	1.5 min
Sample Size	1 μ l

Procedure for Extraction of Tar

1. Hexane Extraction

To 30.19 grams of tar #102 from Pilot Plant Run No. 102 (temperature 550°C) was added 141.44 grams of hexane, HPLC grade, from Caledon Laboratory. Solution was refluxed for 4 hours and then filtered. 3.51 grams went into solution, that is, 11.6% of tar.

2. Toluene Extraction

300 grams of toluene, Canlab - purified, was applied to the residue from the hexane extraction step. The solution was refluxed for 7 hours and then filtered. 3.71 grams of the residue went into solution, that is, 12.3 wt % of initial tar. Insoluble residue was 76.1% of the original tar. Samples of the hexane soluble and toluene soluble fractions were taken for GC/MS analysis.

Figure 4.21

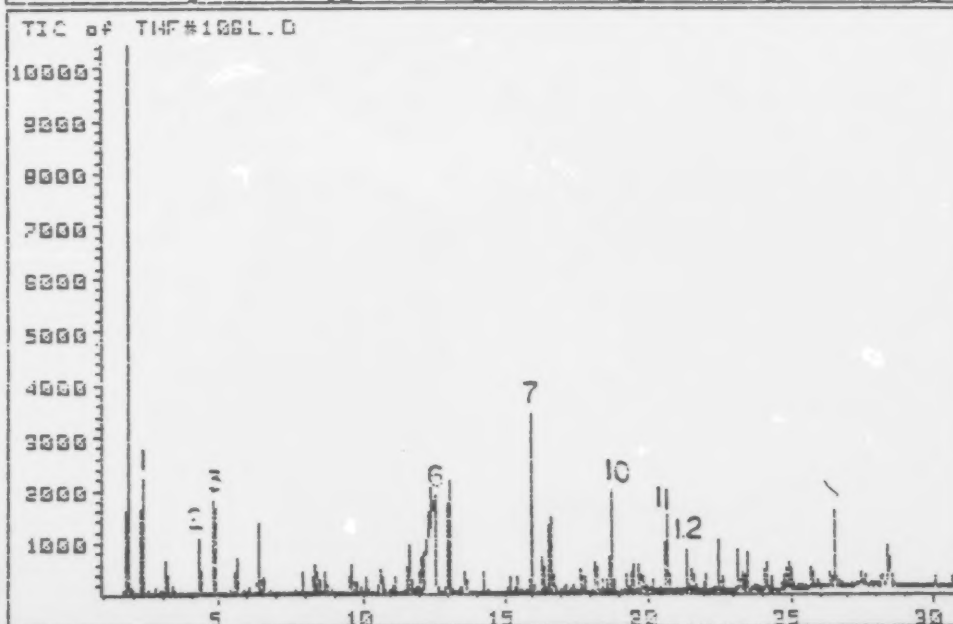
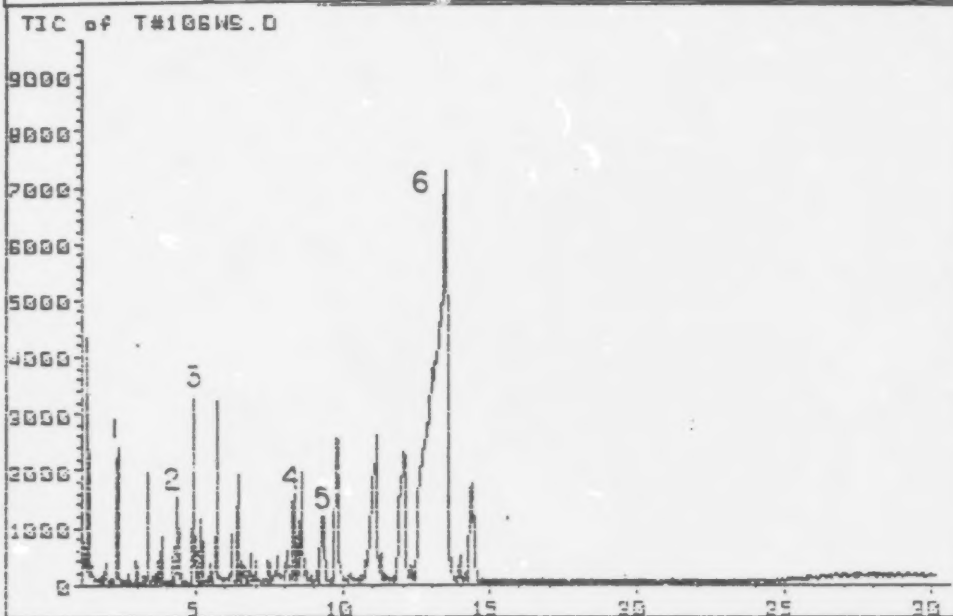
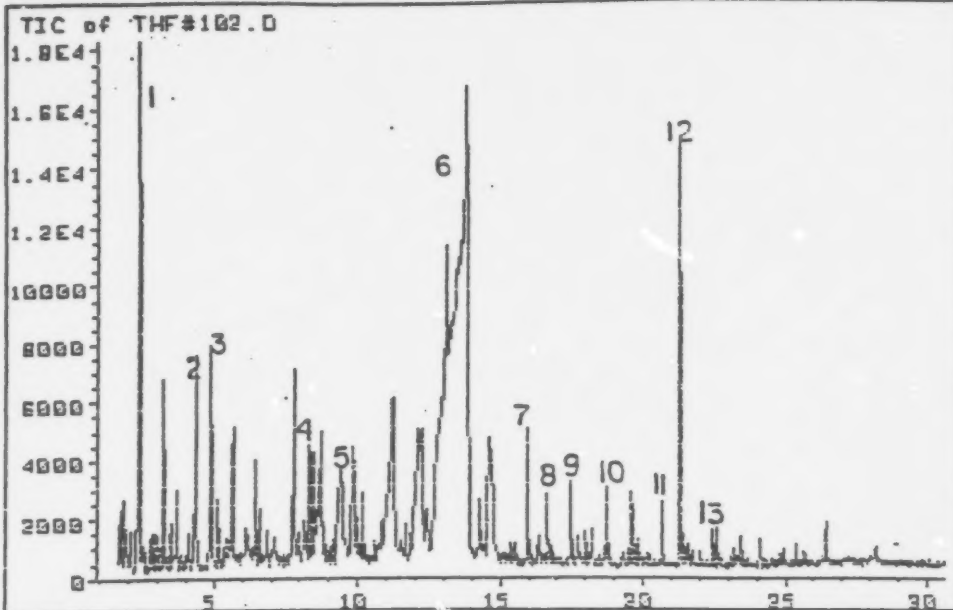
GC/MS Results

Run 102, 550°C 68

TAR

TAR
water soluble

TAR
water insoluble



soluble materials were also subjected to GC-MS analysis. Spectra are shown in Figure 4.22, and the extraction procedure is also given in Table 4.14.

Major peaks in the various spectra, labelled from 1 to 13, are tentatively identified in Table 4.15, together with preliminary identification of a number of minor components. Compounds from 1 to 6 are water soluble, some also hexane soluble. Compounds from 7 to 13 are long chain hydrocarbons or are aromatic in nature. In particular, the long chain hydrocarbons constitute a considerable fraction of the hexane solubles. The nature of these components suggest that upgrading of this oil to a gasoline range product might be feasible, given the lower oxygen content of these tars (about 33%).

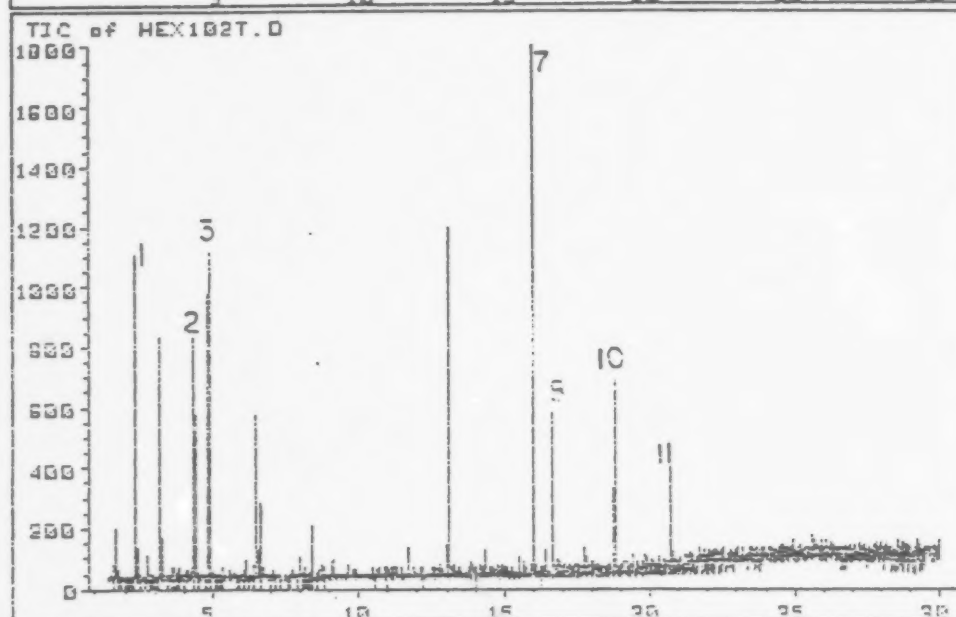
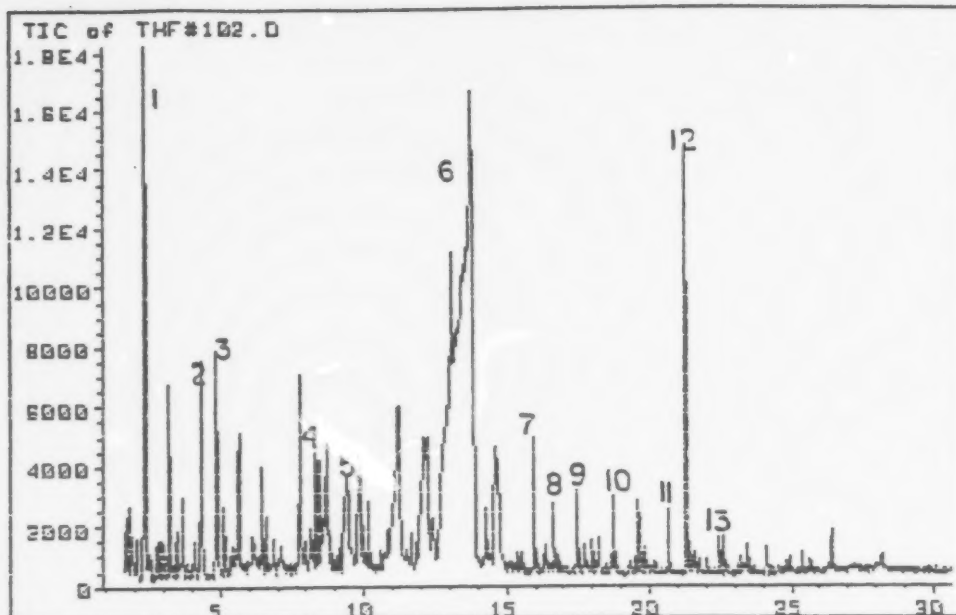
Figure 4.22

GC/MS Results

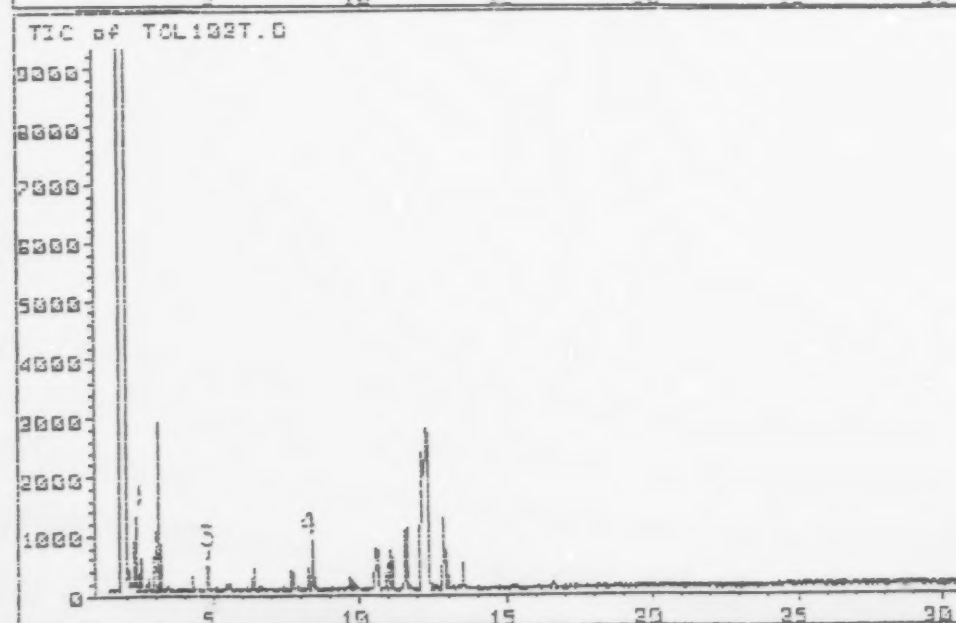
70

Run 102, 550°C

TAR



TAR
hexane soluble



TAR
toluene soluble

Table 4.15

Gas Chromatography - Mass Spectrometry of Tar from Run 102

Identification of Major Peaks (tentative):

1. Furfural
2. Methylfurfural
3. Phenol
4. 1-2 Benzenediol
5. Xanthosine
6. Levoglucosan
7. 1-Nonanol, 4,8-dimethyl
8. 1-Eicosene
9. 4-Morpholinebutanoic acid, "alpha"
10. 1-Nonadecene
11. 11-Tricosene
12. 1,2-Benzenedicarboxylic acid, 2-butoxyether
13. 1-Hexacosene

Minor Peaks Detected	R.T.(min)
2 (3 H) Furanone, dihydro	3.1
p-Cresol	6.2
2-cyclopentene 1-one, 2,3,4 trimethyl	6.6
Phenol, 4 ethyl	7.9
Benzene, 1,4-dimethoxy	8.3
5-Hydroxymethylfurfural	8.5
Benzofuran-2,3 dihydro	8.7
1,2 Benzenediol, 3-methyl	9.0
Ethanone-1-(2-hydroxy, 5-methylphenyl)	10.1
Benzaldehyde, 4-hydroxy, 3-methoxy	11.1
Phenol-2 methoxy-5-(1-propenyl)	12.0
Phenol 2,6-bis (1,1-dimethylethyl)-4 methyl	13.1
[1,1'-Biphenyl]-3 ethoxy	15.2
1-Heptanol 6-methyl	15.5
Dodecanol 3,7,11-trimethyl	15.9
9-Tricosene	18.8
1-Docosanol	22.4
Hexadecanal	23.5
2-Heptadecanone	25.0
Undecan 5-cyclohexyl	25.7
2-Pentadecanone	26.6

4.3 Pyrolysis of Low Grade Peat (Premier)

4.3.1 General Description of Peat Feedstock

This peat originated from a deposit near Rivière-du-Loup, Québec, and is designated as "Premier" brand peat by the producer, Premier Peat Moss Co. Ltd. of Rivière-du-Loup, Québec. It is a highly degraded black, sphagnum high moor peat of the type generally classed as fuel peats.

Ash was determined by the oven method, in which a dry sample is combusted slowly at 700°C. Ash content was found to be 2.32 wt % mf. Elemental C/H/N analysis was carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario with the results listed below.

	wt % mf		
	Sample 1	Sample 2	Average
Carbon	51.47	52.69	52.08
Hydrogen	5.50	5.63	5.56
Nitrogen	1.37	1.40	1.38

4.3.2 Pilot Plant Experiments

Pilot plant tests were carried out according to procedures described in Section 3. The following range of parameters was covered by the pyrolysis tests:

Temperature, °C	457 to 647
App. Residence Time, s	0.44 to 0.55
Feed Rate, kg/h	1.45 to 3.30
Moisture Content, wt %	9.0 to 38.9

Results are summarized in Table 4.16 and in Figures 4.23 and 4.24. No operating difficulties were experienced in feeding this black peat, or in collecting the products. However, moisture contents greater than 40% would probably cause some difficulties with the screw feeder because of the cohesiveness of the wet black peat.

The results for the Sogevex high quality sphagnum peat are plotted together with the yields for the Premier black peat in Figures 4.23 and 4.24. Gas yields were nearly identical for the two peats, while char yield was higher by 3% to 5% for the black peat, and organic liquid yields lower by 7% to 8% at the optimal temperature of 525°C. In the optimal range, product water yield was about the same for both peats, around 10%. Considering the differences in physical nature of the two peats, the pyrolysis results are surprisingly similar. It can be inferred that most intermediate peats would give very similar results.

Table 4.16

Premier Peat - Results of Pilot Plant Pyrolysis Tests

Pilot Plant Run	113	111	112	114	115
Premier Peat Run	3	1	2	4	5
Temperature, °C	457	503	545	600	647
App. Residence Time, s	0.50	0.55	0.45	0.50	0.44
Feed Rate, kg/h (as is)	3.30	1.69	2.31	2.11	1.45
Amount Fed, grams (as is)	4225.4	3809.6	3848.7	3166.9	2568.3
Moisture, wt %	12.2	38.9	17.0	9.0	18.2
Yields, wt %, mf					
Gas	10.95	15.28	15.49	21.67	29.13
Char	40.46	34.27	30.80	27.24	28.32
Water	8.42	9.57	11.10	12.53	8.57
Organics	36.22	39.54	39.28	35.26	31.94
Total	96.05	98.66	96.67	96.71	97.95
H ₂	-	0.02	0.02	0.10	0.12
CO	2.20	3.28	4.70	9.65	12.91
CO ₂	8.19	10.94	9.22	8.63	10.61
CH ₄	0.16	0.37	0.48	1.28	1.99
C ₂ H ₄	0.06	0.20	0.20	0.54	0.95
C ₂ H ₆	0.02	0.04	0.09	0.18	0.38
C ₃	0.04	0.08	0.15	0.20	0.41
C ₄ ⁺	0.28	0.34	0.64	1.09	1.76

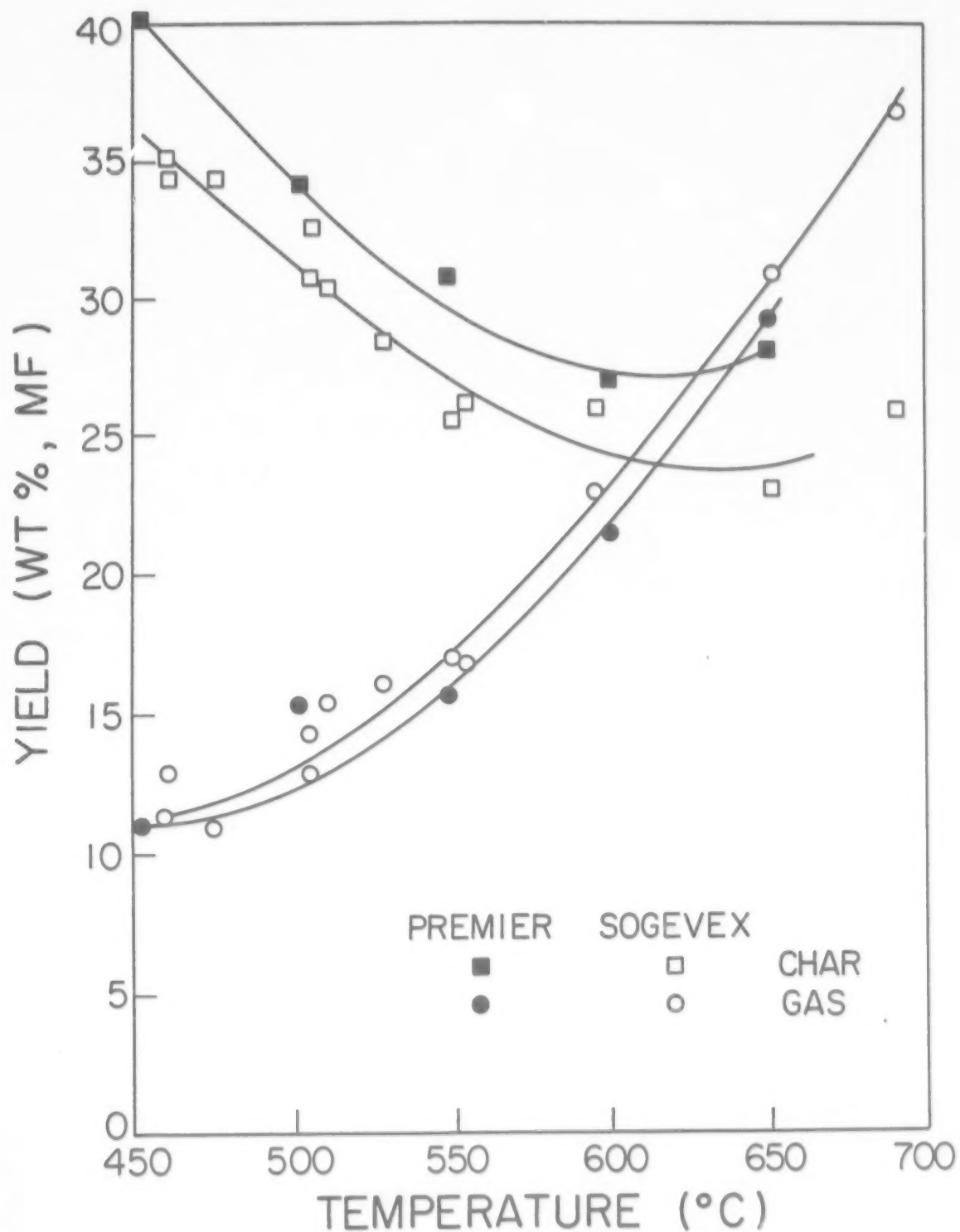


Figure 4.23 Comparison of Yields of Char and Gas for Premier (black) Peat and Sogevex (brown) Peat

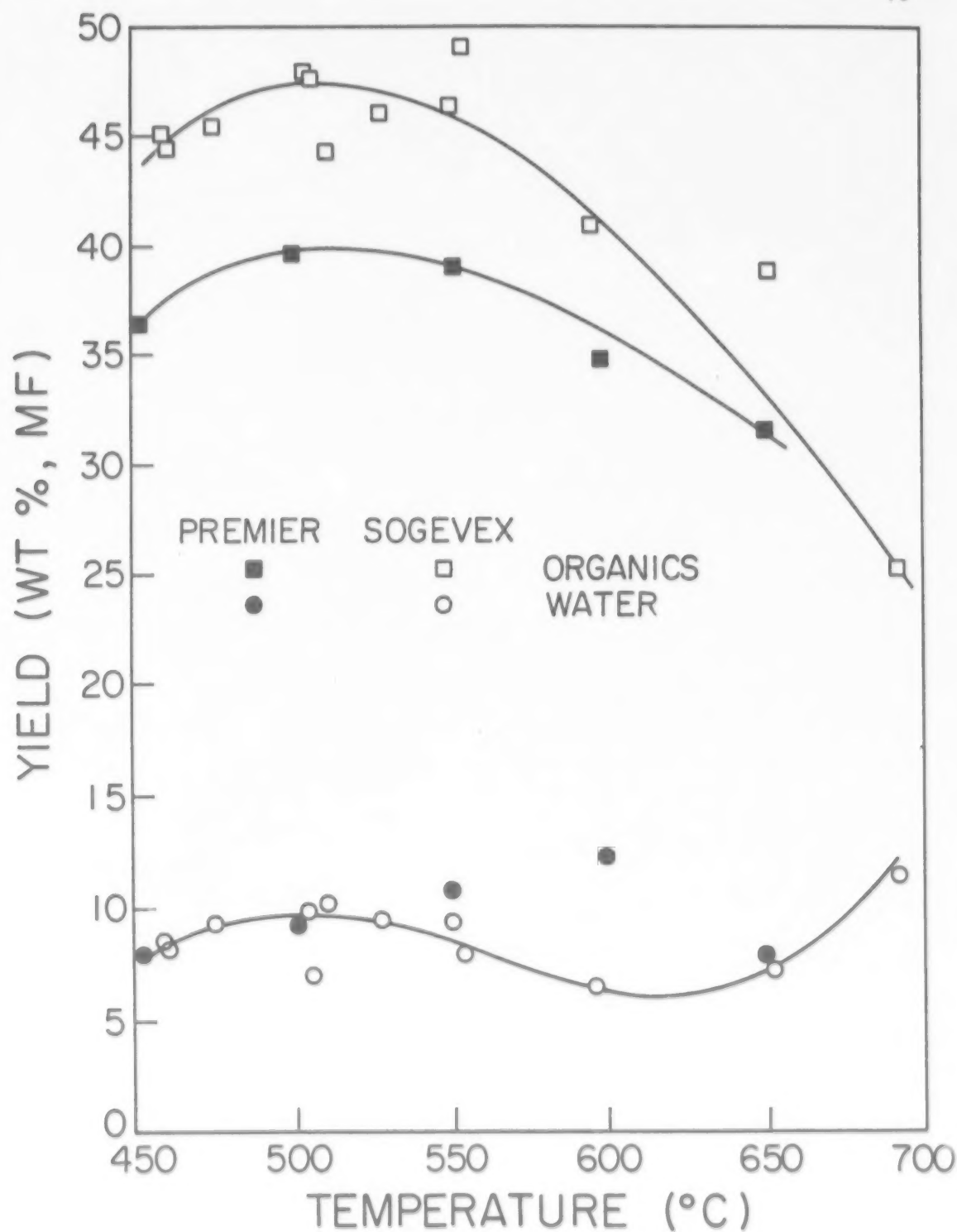


Figure 4.24 Comparison of Yields of Organic Liquid and of Water for Premier (black) Peat and Sogevex (brown) Peat

4.3.3 Chemical Analysis of Pyrolysis Liquids

1. High Performance Liquid Chromatography

The previously described HPLC technique was used to analyze the pyrolytic liquors and the water extracts of the tars.

A summary of determinations of yields of water soluble chemicals is given in Table 4.17 and plotted in Figure 4.25 for both the Premier and Sogevex peats. The remarkable change in the ratio of water soluble to water insoluble products observed for Sogevex peat also occurs with Premier peat, except that for the latter the ratio continues to decrease steadily as temperature increases. The reduction in liquid yields at high temperatures (600° to 650°C) for the Premier peat, occurs almost entirely at the expense of water soluble components.

2. Hexane Extraction

To 34.9 grams of tar #112 from the test at a temperature of 545°C was added 134.9 grams of hexane, HPLC grade (Caledon). The solution was refluxed for 4 hours and then decanted; 8.06 grams of tar went into solution (hot), that is 23.09 wt % of the original tar sample. Visible precipitation was observable after cooling the solution to room temperature. This precipitate (see next

Table 4.17

Results of HPLC Analysis of Water Soluble Chemicals

Pilot Plant Run	113	111	112	114	115
Temperature, °C	457	503	545	600	647
Yields, wt % feed, mf					
Organic Liquid	36.22	39.54	39.28	35.26	31.94
Water Insoluble	11.26	18.24	20.44	19.89	19.55
Water Soluble	24.96	21.30	18.84	15.37	12.39
Water Soluble Components, wt % feed, mf					
Oligosaccharides	0.23	0.13	0.17	0.10	0.06
Cellobiosan	1.19	0.60	0.98	0.58	0.24
Glucose	1.81	0.36	0.37	0.23	0.03
Fructose (?)	1.44	0.83	0.80	0.62	0.34
Glyoxal (?)	0.65	0.49	0.60	0.65	0.27
1,6-Anhydroglucofuranose	0.99	0.56	0.58	0.45	0.26
Glyceraldehyde	1.59	1.00	0.93	0.74	0.46
Levogluconan	7.83	4.59	5.17	5.05	3.23
Hydroxyacetaldehyde	-	1.24	0.81	0.81	1.23
Formic Acid	2.27	0.89	0.39	0.25	-
Formaldehyde	-	-	0.38	0.25	0.42
Acetic Acid	1.92	1.50	0.77	1.04	0.86
Acetol	0.27	0.66	0.22	0.37	0.32
Total	20.19	12.85	12.49	11.14	7.72

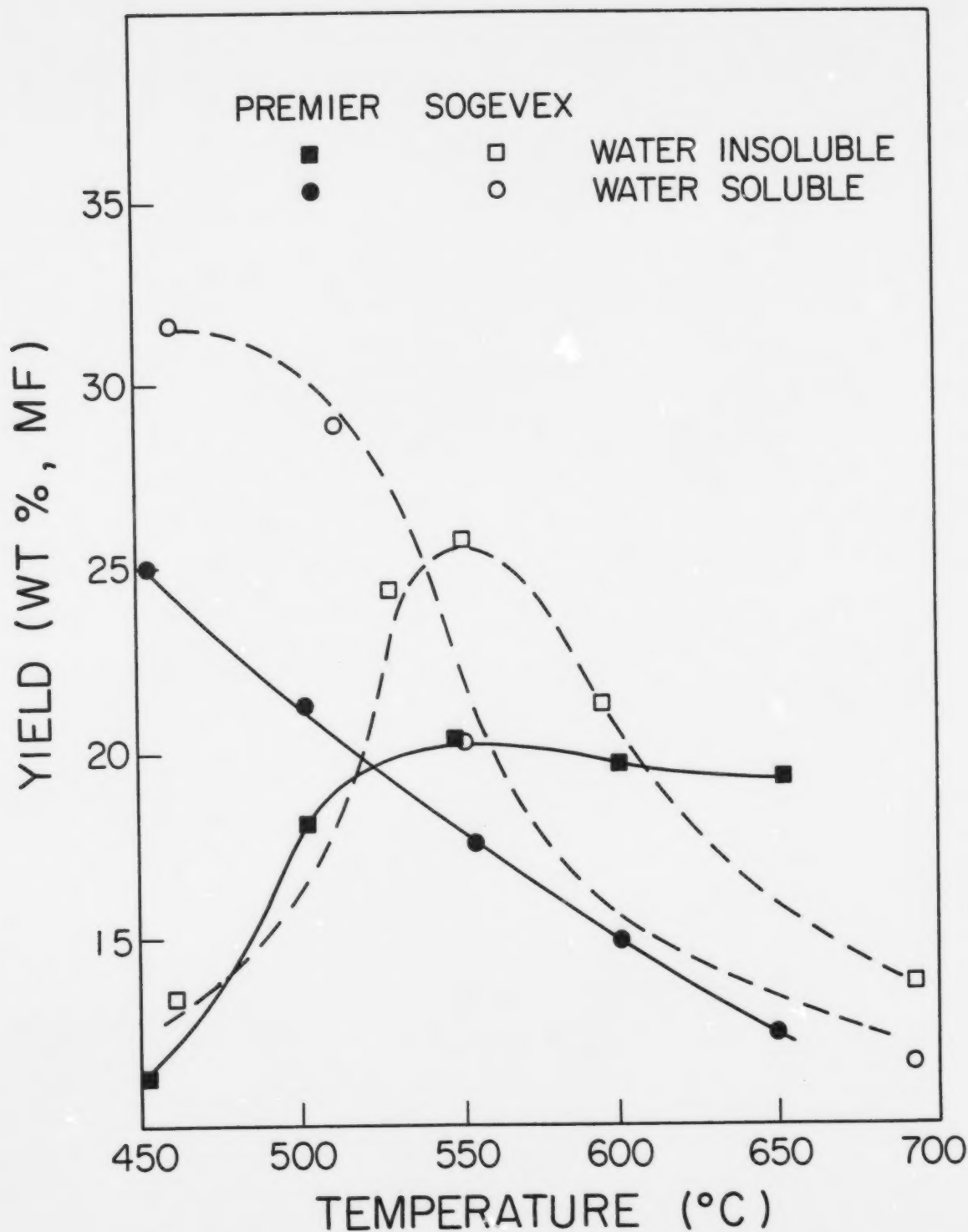


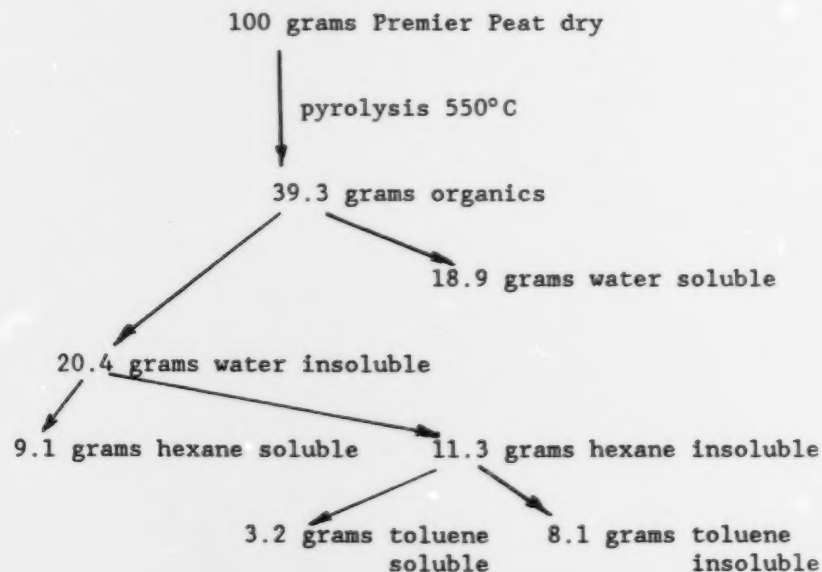
Figure 4.25 Yields of Water Soluble and Water Insoluble Liquid Fractions from Premier and Sogevex Peats

section) is almost certainly long chain normal paraffin wax components.

3. Toluene Extraction

258.4 grams of toluene, Canlab-purified grade, was added to the residue from the hexane extraction step. The mixture was refluxed for 8 hours, then the liquid was decanted from the solids. 2.85 grams of the tar residue went into solution, that is, 8.16 wt % of initial tar sample.

A visualization of the water, hexane and toluene extraction steps is shown below for tar fraction #112, with the results given previously.



4.3.4 Gas Chromatography - Mass Spectrometry Analyses

Tar from test #112 was also selected for further analysis using the GC-MS technique. In addition to analysis of the whole tar, the hexane and toluene soluble fractions of this tar were also characterized by GC-MS.

The apparatus used and conditions for the analyses are listed below.

GC-MS Equipment:

H-P 5890 Gas Chromatograph

H-P 5970 Mass Selective Detector

H-P Crosslinked methyl-silicone capillary column

Parameters of GC-MS Analysis

Scanning Range	20 - 450 amu
Initial Temperature	60°C
Initial Time	2 min
Ramp Rate	10 deg/min
Final Temperature	250°C
Transfer Line Temperature	250°C
Injection Port Temperature	250°C
Solvent Delay	1.5 min
Sample Size	1

The total ion chromatographs of the three samples analyzed are shown in Figure 4.26. Major peaks tentatively identified are listed in Table 4.18.

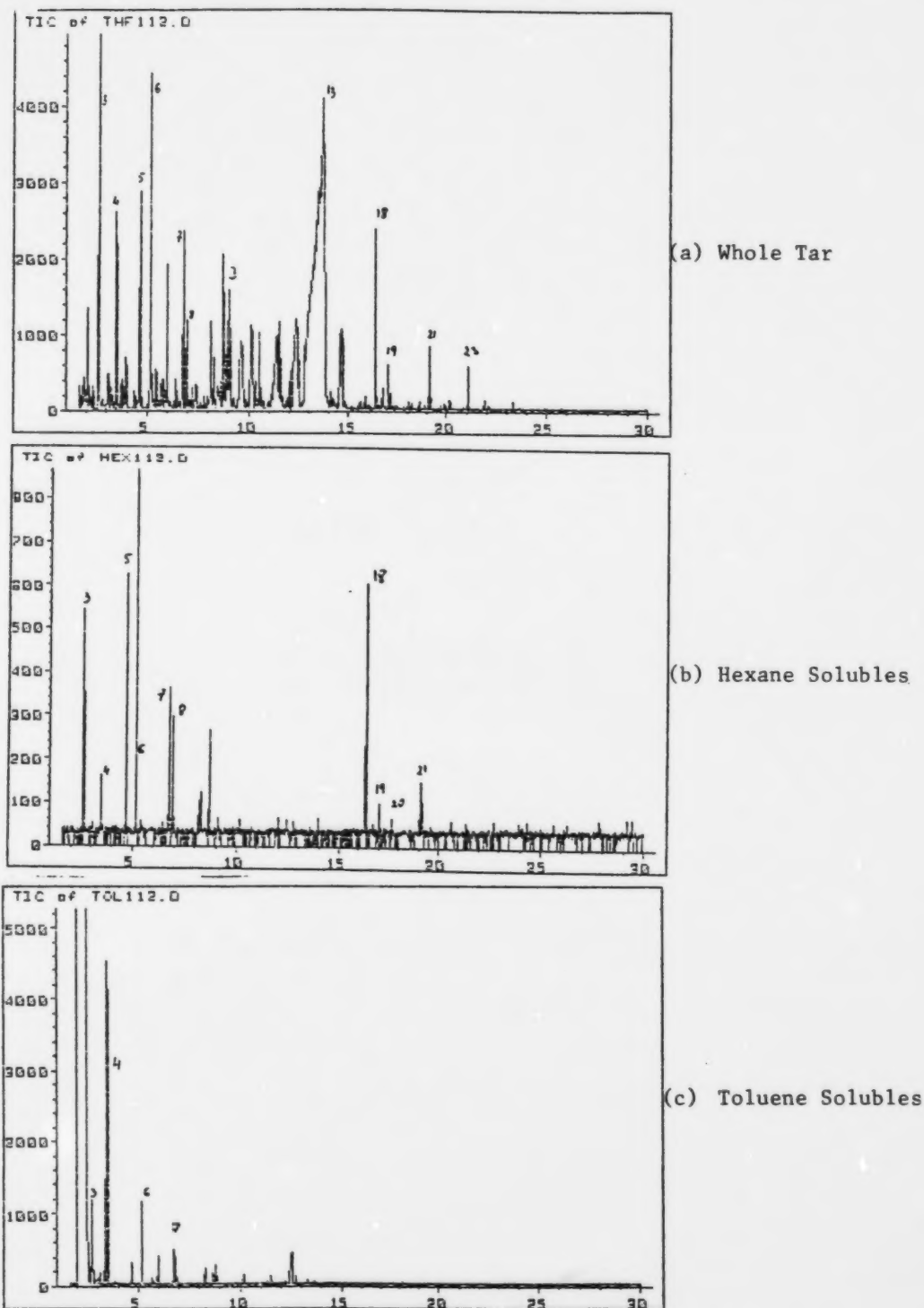


Figure 4.26 GC-MS Results for Tar No. 112 from Pilot Plant Pyrolysis of Premier (black) Peat at 545°C, 0.45 s
 (a) whole tar (b) hexane soluble portion of water insolubles (c) toluene soluble fraction after removal of water and hexane solubles

Table 4.18

GC-MS Identification of Major PeaksPeak Number

3	Furfural
4	?
5	Methylfurfural
6	Phenol
7	Phenol, 4-methyl
8	2-Cyclopenten-1-one, 2,3,4 trimethyl
9	Methylglyoxal
10	Ethanone-1-(2-hydroxy-5 methylphenyl)
13	Levoglucosan
18	1-Nonanol, 4,8-dimethyl
19	11-Tricosene
23	1,2-Benzenedicarboxylic acid, 2-butoxyether
21	} 1-Nonadecene
20	

4.3.5 Elemental Analyses of Products

The elemental analyses of chars and tar products are presented in Table 4.19. As expected, the C content of char increases and the H content decreases as temperature increases. Results for the tars are not as consistent, probably due to the difficulties of micro-sampling the rather heterogeneous liquid product. However, there appears to be a trend to

Table 4.19

Elemental Analysis of Pyrolysis Products*

Pilot Plant Run No.	113	111	112	114	115
	CHARS				
Carbon	64.73	64.93	65.34	69.63	73.22
Hydrogen	4.00	3.58	2.99	2.91	2.86
Nitrogen	1.56	1.29	1.30	1.22	1.10
	TARS				
Carbon	61.73	71.52**	58.09	58.56	59.13
Hydrogen	8.95	9.29	7.62	7.21	6.89
Nitrogen	1.10	0.77	1.43	1.85	2.15

* Analysis done by Guelph Chemical Laboratories, Guelph, Ont.

** Numbers not very realistic!?

lower hydrogen and higher oxygen contents as temperature increases, which may reflect the removal of hydrocarbon side chains or increased aromatization.

Carbon and hydrogen balance calculations are given in Table 4.20 for one run (Run 112, 545°C). Results are satisfactory with closure of overall, carbon and hydrogen balances to the range of 95% to 100%, giving support to the validity of the analytical data presented.

A summary is shown in Table 4.21 of results for three Quebec sphagnum peat mosses of different degrees of degradation (ET peat, a high quality long fibre sample obtained from Dr. Bernard Coupal, believed to be from a deposit in the Eastern Townships, Sogevex brown peat and Premier black peat). Carbon content increased slightly and hydrogen content decreased as the quality degraded. Pyrolysis results showed significantly greater char yields and correspondingly reduced organic liquid yields as quality decreased (23% vs. 34% and 57% vs. 40%, respectively). These trends are as would be expected, except that organic liquid yields from the long fibre peat are surprisingly high (56.8%). However, tar yields from the low grade black Premier peat are still surprisingly good in view of the quality of this feed stock -- sufficiently high that almost any peat could be considered as a potential feed for the Waterloo Fast Pyrolysis Process.

Table 4.20

Carbon and Hydrogen Balances - Premier Peat Run No. 112

Peat - Chemical Analysis (Sample 1)	Carbon	51.47 wt % mf
	Hydrogen	5.50 "
Char #112	Carbon	55.34 "
	Hydrogen	2.99 "
Tar #112	Carbon	58.09
	Hydrogen	7.62

Yields, Run #112, wt % mf

		Carbon	Hydrogen
Char	30.8	20.12	0.92
Tar	39.28	22.82	2.99
Water	11.1	-	1.23
H ₂	0.02	-	0.02
CO	4.70	2.01	-
CO ₂	9.22	2.51	-
CH ₄	0.48	0.36	0.12
C ² H ⁴	0.20	0.17	0.03
C ² H ⁶	0.09	0.07	0.02
C ³	0.15	0.13	0.02
C ⁴	0.64	0.55	0.11
		48.74	5.46
Recovery	96.67	94.7%	99.3%

Table 4.21

Summary of Analyses and Pyrolysis Yields at 500°C
for Three Quebec Sphagnum Peat Mosses

	ET Moss (Coupal)	Sogevex	Premier
<u>Ash</u> , wt %, maf	4.7	3.7 (3.9)	2.3
<u>Elemental Analysis of Peats</u> , wt % maf			
Carbon	48.10	51.40 (48.8)	52.08
Hydrogen	5.88	5.61 (5.72)	5.56
Nitrogen	1.44	1.35 (1.14)	1.38
Sulphur	N.D.	- (0.12)	N.D.
<u>Pyrolysis Yields</u> , wt % maf			
Run Number	Bench Unit	101	111
Char	22.78	30.75	34.27
Gas	13.47	14.26	15.28
Water	7.77	9.80	9.57
Organics	56.78	47.80	39.54
Total Recovery	100.8	102.6	98.66

() - Results from Central Research Laboratory, Finland

5. INCIDENTAL RESULTS

5.1 Incidental Results

A sample was prepared at the request of IEA from the Canadian peat (Sogevex) and a quantity of two litres was obtained by combining tars from Runs 101 and 106 (505°C and 511°C, respectively). The averaged conditions and yields for the two runs are given in Table 5.1. This sample will be given preliminary upgrading tests using the PNL-Battelle fixed bed reactor with a sulfided CoMo catalyst, presumably at conditions found to be suitable for oils such as the PERC wood-derived oil. The results of these upgrading tests will be reported by the IEA task force in their updated report on the IEA Biomass Liquefaction Test Facility.

5.2 Thermogravimetric Tests

In order to establish the value of TGA analysis as a means of determining the pyrolysis behaviour of an unknown peat sample, a standard TGA comparison was made of all the peat samples available to us.

The results of this analysis of seven samples are plotted in Figure 5.1 with explanatory information concerning analytical conditions and sample identification compiled in Table 5.2. An examination of these curves shows the higher yield of volatiles from the younger peats, which corresponds to a

Table 5.1

Pilot Plant Run 101/106, Sogevex Peat
(moisture 19.1 wt %)

Temperature 509°C
App. Residence Time 0.48 seconds

Yields, wt % mf

Gas	15.08
Char	30.44
Water	10.03
Organics	45.08

H ₂	0.02
CO	4.15
CO ₂	9.8
CH ₄	0.48
C ₂ H ₄	0.17
C ₂ H ₆	0.07
C ₃	0.09
C ₄ ⁺	0.32

Tar Analysis, wt % of Total Tar
(aqueous phase not incl.)

Elemental Analysis
(wet basis 12.8% water)

Water	12.8	Carbon	51.62
Oligosaccharides	0.16	Hydrogen	7.65
Cellobiosan	1.83	Nitrogen	1.91
Glucose	0.72		
Mannose	2.43		
Glyceraldehyde(?)	2.41		
Levogluconan	12.04		
Acetic Acid	0.99		
Acetol	0.21		
Water Soluble	68		
Water Insoluble	32		
Hexane Soluble	11		
Hexane, Toluene Soluble	23		

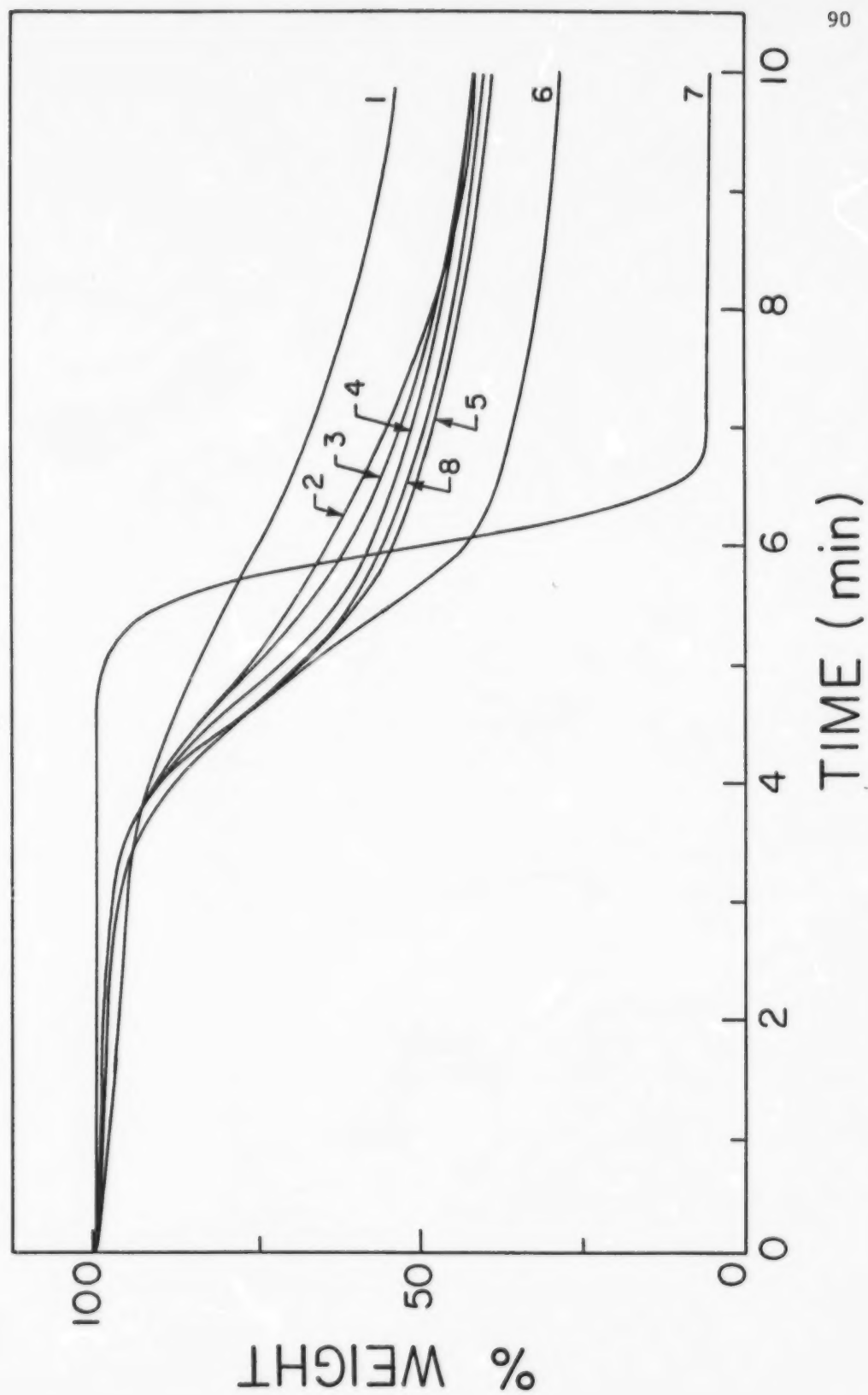


Figure 5.1 TGA Results for Different Peats and Cellulose
(see Table 5.2 for key)

Table 5.2Thermogravimetry Test Conditions

Equipment : Perkin-Elmer TGS-2

Atmosphere : N₂

Sample Size : 3 to 4 mg

Program Used

Initial Temperature : 100°C held as long as weight loss due to water removal visible.

Ramp Rate : 50 degrees per minute up to 600°C.

<u>Curve Identification for Figure 1</u>		<u>Max. Org. Liquid</u>
		<u>Yield % mf</u>
1. Negril peat (Jamaica)		20
2. IEA peat (Finland)	} Sphagnum Type	41
3. Pit Moose peat		-
4. Premier peat		-
5. Sogevex peat		47
6. Moss, peat moss (Coupal 1985)		-
7. Avicel 102		87
8. Namsco peat		-

higher yield of condensable organics in fast pyrolysis. The contrasting behaviour of Avicel, a pure microcrystalline cellulose, also illustrates the complex and heterogeneous nature of peat, particularly older peats.

6. UPGRADING TESTS

by Jan Piskorz and Peter Majerski

6.1 Introduction

The successful attempts to pyrolyze Canadian peat in the Waterloo Flash Pyrolysis pilot plant unit generated a product tar in amounts sufficient to allow undertaking some preliminary upgrading experiments.

It was thought that a batch autoclave system would be the primary tool in such testing, but after three rather unsatisfactory experiments the details of the then unpublished work of Elliott [9] became known to the authors of this report (who are also co-authors of Elliott's communication).

The novel, quite pioneering, set of data delivered by Elliott gave us the impulse and courage to build a continuous high pressure unit modified from the design used by Elliott, and all succeeding experiments were performed in this new apparatus.

The desire to bring our experimental upgrading setup to a higher standard of laboratory engineering caused some delay in the completion of the proposed tests.

6.2 Background

To obtain hydrocarbons from highly oxygenated primary pyrolytic tars from wood or peat, the heteroatoms, in this case almost entirely oxygen, have to be removed in the process of hydrotreatment. Removal of heteroatoms like nitrogen, sulphur and some metals is routinely done in petrochemistry in various refining processes called

HDS ---> hydrodesulphurization

HDN ---> hydrodenitrogenation

HDM ---> hydrodemetalization.

Oxygen removal by the same type of process has only recently received some attention due to the upgrading of tars originating from coal [1].

Hydrodeoxygenation investigations of model compounds have been reported by Furimsky, of furan, tetrahydrofuran [2], LaVopa of dibenzofuran [3] and by Shabtai of diphenylether [4]. Those researchers [2],[3],[4] used as a catalyst sulfided cobalt molybdena on alumina, one of the standard catalysts employed in petrochemistry. More exotic catalysts, such as ruthenium and Raney nickel were tried by Piskorz and Scott [5] to upgrade wood-derived oil. The work of Elliott et al. [6][7][8] describes not only hydrotreatment of model compounds but also hydrodeoxygenation of "real" pyro-liquids from wood. His is the most relevant work to date concerning up-grading of peat-tar [9].

Major conclusions by Elliott et al. are:

- A. Tar obtained from flash pyrolysis of peat can be upgraded to almost entirely hydrocarbons (oxygen content 1.5% wt) in a gasoline boiling range (86% wt boils below 225°C) in a continuous high pressure (13.8 MPa) process using commercial cobalt-molybdena catalyst over a temperature range of 300° to 400°C with a liquid space velocity of 0.19 vol. feed/(vol. catalyst)/(hr).
- B. The major classes of chemicals in the final product reported by Elliott were cyclohexanes, aromatics and long chain n-alkanes.

The principal aim of this work was to obtain first hand experience in conducting upgrading tests and, to some degree, to confirm the findings of Elliott et al.

6.3 Upgrading Tests - Experimental

6.3.1 Catalysts Used

The list of catalysts used in the deoxygenation trials is given in Table 6.1. Cobalt and nickel commercial catalysts were selected. Sulfiding of these catalysts was performed in-house using 10% by volume H₂S in a stream of H₂.

Additional information about these catalysts is also given in the Appendices.

Table 6.1

Description of Catalysts Used

-
- Catalyst A : $\text{NiO} : \text{MoO}_3 : \text{Al}_2\text{O}_3$ ---> nickel oxide on molybdena and alumina from United Catalyst Inc. Minus 250 μm particle size fraction used in its oxide form. See also Appendix 1.
- Catalyst B : CoMo-0401 ---> CoO , MoO_3 , Al_2O_3 from The Harshaw Chemical Co. Minus 150 μm particle size fraction used. Catalyst used in its sulfided form after treatment at 480°C , for 5 hours with 10% H_2S in H_2 .
- Catalyst C : CoMo-0401 ---> -20 +40 mesh (0.84-0.42 mm) oxide form used.
- Catalyst D : KATALCO 499 ---> $\text{CoO} - \text{MoO}_3$ on alumina from Katalco Corporation (see Appendix 2). Sulfided in-house with 10% H_2S in H_2 at 440°C .
- Catalyst E : KATALCO 502-S ---> nickel-molybdenum catalyst (see Appendix 3). Used in sulfided form as above.
-

6.3.2 Feedstocks

The following pyrolytic tars were chosen for catalytic treatment.

Table 6.2

Feedstock Characteristics

Sample No.	Peat Source	Pyrolysis Temp. $^\circ\text{C}$	Yield wt %,mf	Elemental Analysis	
				Carbon	Hydrogen
T #88	Sogevex	554	48	56.6	6.99
T #103	Sogevex	460	45	52.3	6.55
T #113	Premier	457	36	-	-

Tar T #113 contained 24% wt water. Other tars were used in their drier state. Additional information about these tars was given in the previous sections.

HPLC analysis of the water soluble chemicals present in Sample T #113 is given in Table 6.3.

Table 6.3
Peat Tar Sample T #133

Compound	w/w % of Total Tar
1. Oligosaccharides	0.49
2. Cellobiosan	2.52
3. Glucose	1.34
4. Fructose	3.04
5. Glyoxal	1.37
6. 1,6 Anhydroglucofuranose	2.10
7. Glyceraldehyde	3.37
8. Levoglucosan	16.55
9. Hydroxyacetaldehyde	tr.
10. Formic Acid	4.80
11. Formaldehyde	n.d.
12. Acetic Acid	4.07
13. Acetol	0.58
14. Methanol	1.92 (ext)
15. Water	24.0

6.3.3 Batch System Upgrading

6.3.3.1 Upgrading Apparatus

The schematic flow sheet of the batch hydrogenation unit is shown in Figure 6.1. The details of the whole system were given in an earlier report (5). The apparatus operated with continuous hydrogen flow but the liquid tar was treated batchwise.

6.3.3.2 Results

The results of three tests carried out in the batch apparatus are summarized in Table 6.4. The first test was performed isothermally with a nickel-molybdenum on alumina catalyst (Catalyst A) at a quite low temperature of 260°C to avoid extensive coking of the thermally-sensitive tar components (see Elliott [6]). Nevertheless, after terminating the experiment the contents of the reactor when cooled were in a solid phase, and the yield of light distillate reached only 5.6% by weight of the original feed.

For the second experiment, it was decided to use a higher pressure of 2000 psi (13.8 MPa). After 60 minutes, the temperature was raised from 260°C to 340°C to simulate Elliott's two stage approach. In this second test, cobalt-molybdena catalyst (Catalyst B) was sulfided before use.

HYDROGENATION UNIT

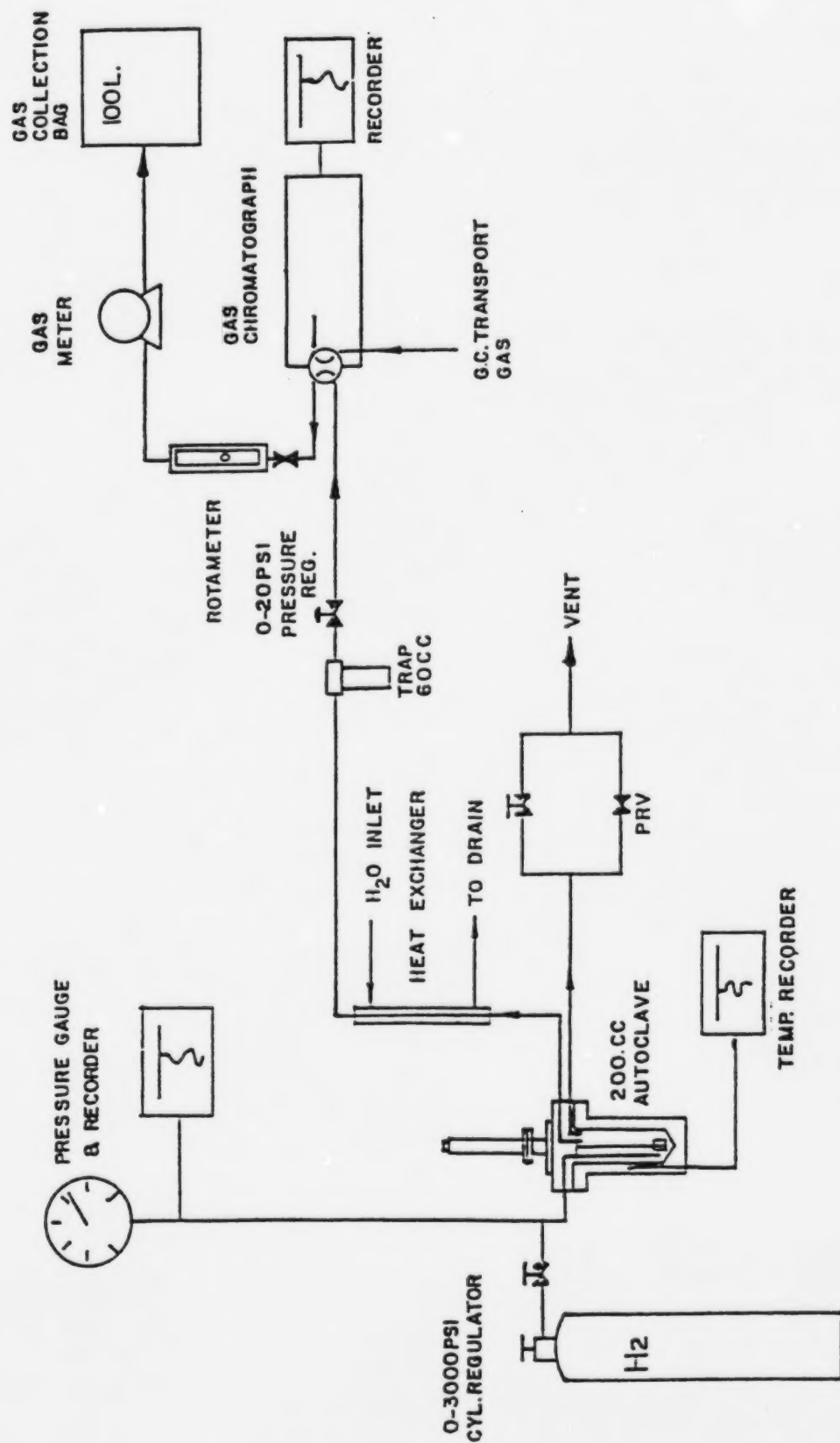


Figure 6.1 Schematic Diagram of Batch Autoclave Pressure Apparatus for Upgrading of Pyrolytic Oil

Table 6.4

Results of Peat-Tar Hydrogenation - Batch System

Run Number	1	8	9
Feed	T #88	T #88	T #103
Amount fed, grams	46.8	51.3	86.6
Catalyst	A	B	B
Amount used, grams	15.	10.	15.6
Temperature - °F	500	500/650	500/650/750
- °C	260	260/340	260/340/400
Pressure - psi	1200	2000	2000
- MPa	8.27	13.79	13.79
Duration, min	135	110	150
Hydrogen Flow (liter STP/min)	0.5	1.0	0.75
YIELDS, grams or (wt% fed)			
Light Distillate (Total)	3.8 (8.1)	18.5 (36.1)	44.1 (50.9)
Water	1.2 (2.5)	13.5 (26.4)	23.8 (27.5)
Organics	2.6 (5.6)	5.0 (9.7)	20.3 (23.4)
Gas			
CO	0.18 (0.38)	0.12 (0.23)	0.21 (0.24)
CO ₂	5.89(12.59)	8.80(17.15)	22.52(26.00)
CH ₄	0.01 (0.02)	0.29 (0.57)	1.66 (1.92)
Others	0.7 (1.50)	1.39 (2.71)	4.39 (5.07)
Residue Inside Reactor	Solidified	THF Soluble	THF Soluble

Solidification on cooling of the contents of the autoclave did not occur in this test, but the yield of light, gasoline-like organics obtained was still relatively low at 9.7 wt % of tar fed.

In the third experiment the final temperature was raised even higher after the first 60 minutes at 260°C, up to 400°C, with results approaching those obtained by Elliott (23.4% versus 32.9%) but with yields of light oil still too low to be classed as fully satisfactory values.

At this point it was decided to abandon the batch autoclave experimentation, because of a lack of adequate control of the temperature-time history of the reaction. Instead, our effort was put into setting up a continuous fixed bed hydro-treating unit modified from that described by Elliott et al. [6][8][9].

6.3.3.3 Conclusions

It is rather difficult to obtain similar results in two dynamically different reaction systems (batch versus continuous) even using similar conditions and catalysts. Therefore, it is not possible to make a direct comparison of these batch results with those obtained by Elliott in a flow reactor. However, these limited results do tend to confirm the necessity of high hydrogen pressure (13.8 MPa), and the

beneficial effect of catalyst sulfidation in improving yields when processing highly oxygenated feedstocks.

6.3.4 Continuous Flow Upgrading

6.3.4.1 Apparatus

The Schematic flow sheet of the continuous hydrogenation unit is shown in Figure 6.2. Details of the tubular reactor vessel are shown in Figures 6.3 and 6.4. The reactor vessel was designed for a maximum allowable working pressure of 13.8 MPa at 400°C. Reactor volume measured from the reactor bottom to the overflow is 96 ml. The two high pressure traps (knock-outs) have a capacity of 58.4 ml and 28.9 ml. The heart of the system is a high pressure liquid chromatography pump, Waters Model 510, able to deliver from 0.25 to 24.0 ml/min of liquid against a pressure of up to 5000 psi (34.5 MPa).

Tars originating from peat are of the consistency of butter, and are freely pumpable only if kept above 60°C. To facilitate the pumpability and controlled rate feeding of such liquids a displacement type reservoir with floating piston (high pressure liquid feeder) was constructed. The HPLC pump metered water into the cylinder on one side of the floating piston, and tar liquid at 60°C was displaced at the same rate from the second chamber of the cylinder. This

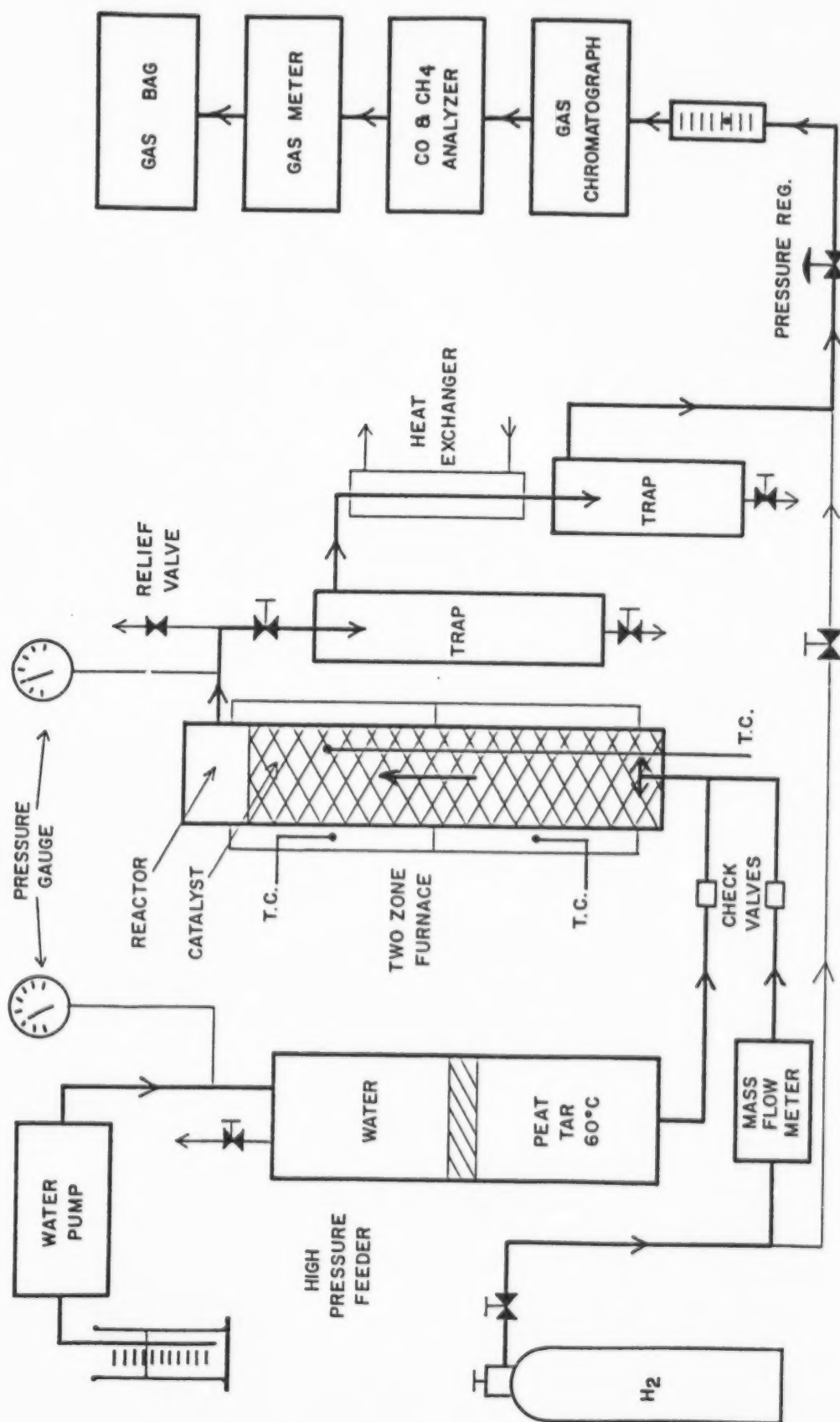


Figure 6.2 Schematic Diagram of Continuous Flow Packed Bed Catalytic Reactor System for Upgrading of Pyrolytic Oil

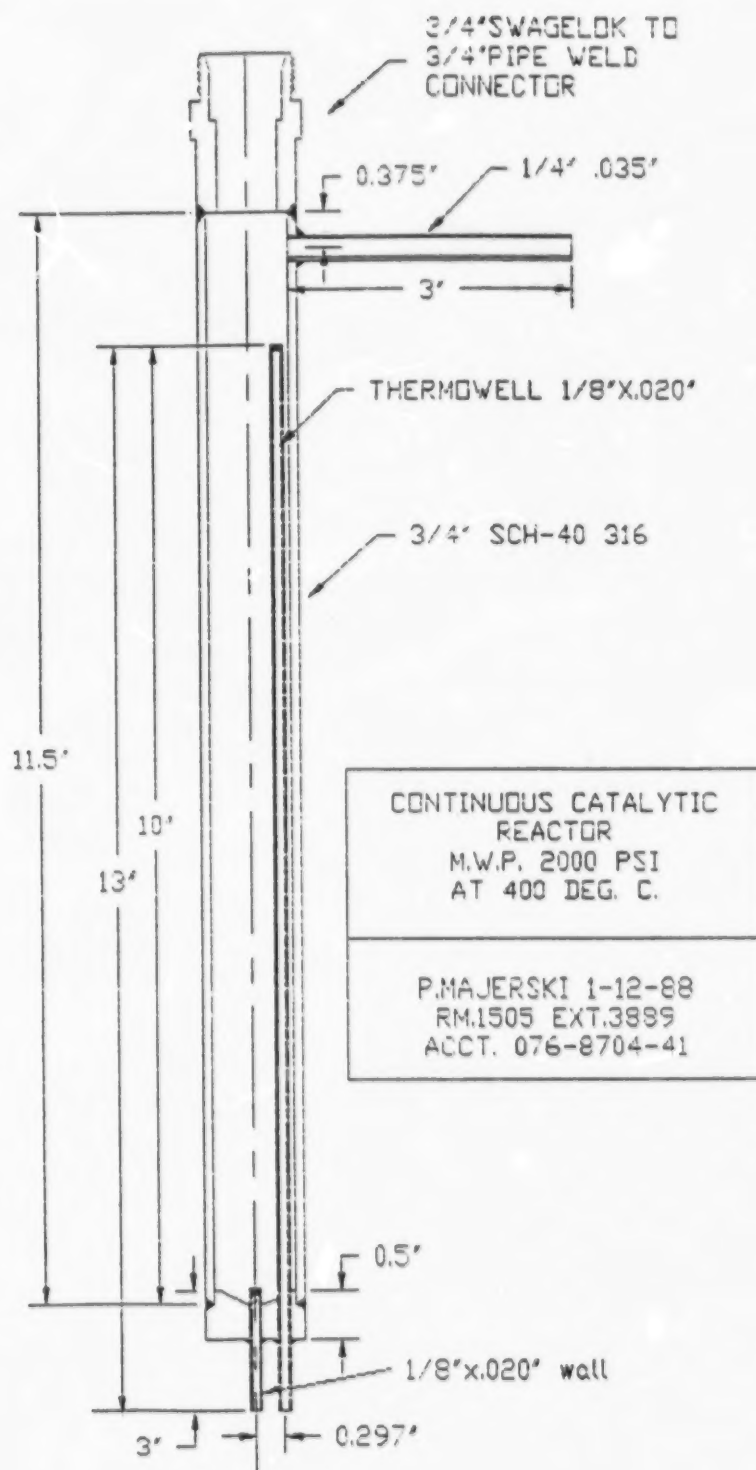


Figure 6.3 Detail of Plug Flow Catalytic Reactor

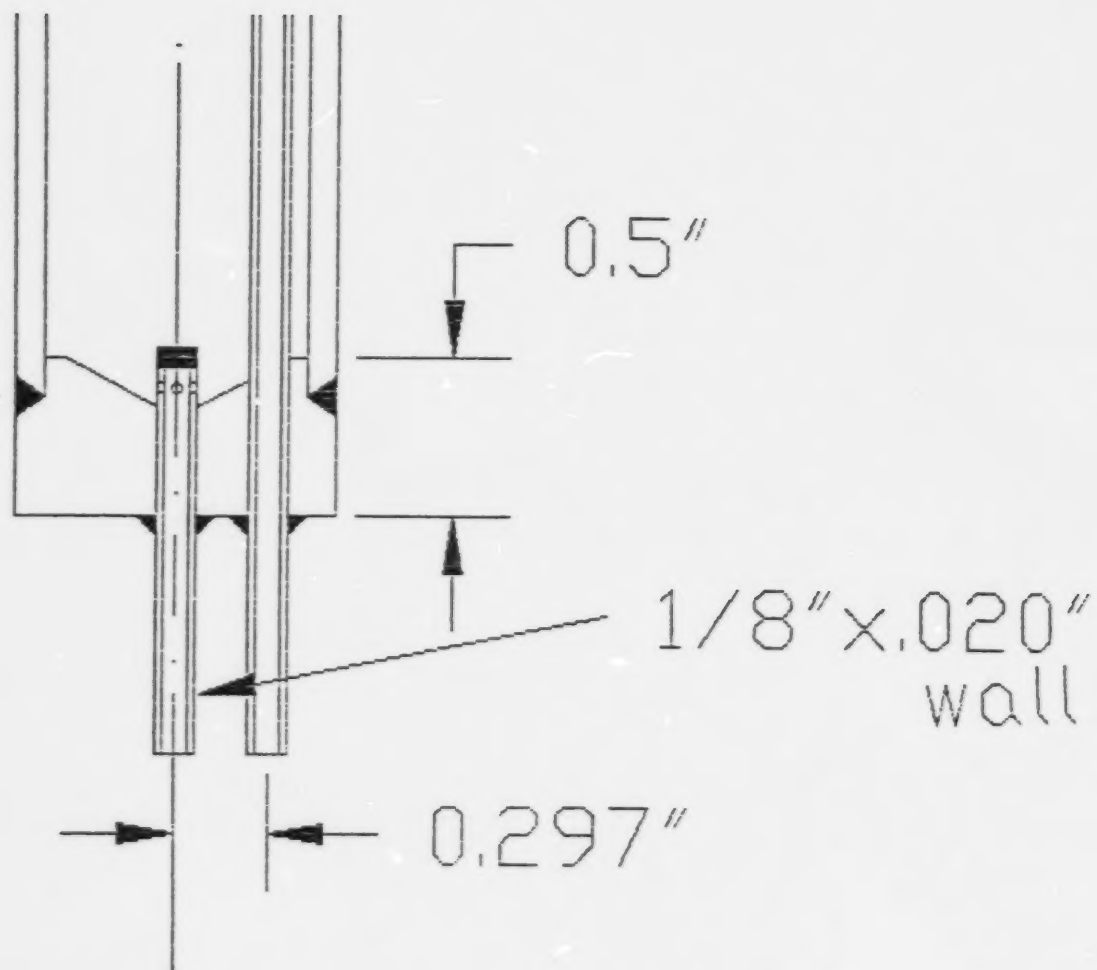


Figure 6.4 Detail of Feed Inlet of Continuous Catalytic Reactor

feeder, having a capacity of 90 ml, was externally heated.

The electric furnace (built in-house) with two independent heating zones contains a specially inserted stainless steel cooling coil which when connected to water coolant can facilitate rapid reactor quenching. Other elements and parts of the continuous unit are identical with the batch system which was described previously.

6.3.4.2 Results

The fixed bed catalytic tests with continuous feed were carried out with tar T #113 as a feedstock. The tar feed rate was kept constant at 0.5 ml/min, or 0.62 gram/min (the density of T #113 [wet] is 1.24 g/ml). For the initial test, it was decided to start experimentation under 7.0 MPa (1000 psi) pressure. Data on other test conditions are given in Table 6.5. In this first run catalyst CoMo-0401 in oxide form (Catalyst C) was used. The run was terminated after 60 minutes because pressure drop across the reactor was increasing steadily. Water was the only product recovered in the condensers. However, all elements of the experimental setup performed well and as expected.

In the second run, to improve permeability of the catalytic bed, Katalco 499 cobalt-molybdenum catalyst on a shaped alumina base was used. The catalyst, after being placed in the reactor, was sulfided in situ with 10% volume H_2S in H_2

Table 6.5

Hydrogenation in Continuous Flow Reactor

Run No.	1	2	3	4	5	6
Catalyst	C	D	D	E	E	E
grams/in oxide form	56.3	66.7	69.9	53.9	56.4	56.4
Temperature °C	340	352	250	270	278	240-380
Pressure, MPa	7.0	7.0	7.0	13.7	13.8	13.7
Hydrogen Flow (STP liter/min.)	0.15	0.39	0.60	0.58	0.5	0.5
Duration, min.	60	84	80	180	180	153
Amount Fed, grams	37.2	52.	49.6	111.6	111.3	90.5
YIELDS, grams						
Light distillate (Total)	16.3 (43.8)	18.8 (36.2)	32.8 (37.7)	44.3 (39.7)	29.9 (26.9)	80.8 (89.3)
Water	16.3	18.8	30.2 (34.7)	36.4 (32.6)	22.2 (19.9)	45.5 (50.3)
Organics	0.0	0.0	2.6 (3.0)	7.9 (7.1)	7.7 (7.0)	35.3 (39.0)
Comments		plugged	plugged			

() = Yield as % of feed, by weight

at 440°C and one atmosphere pressure. This run lasted 84 minutes before the bed became impenetrable for hydrogen flow.

To avoid the high temperature coking and resultant plugging of the catalyst bed the third run was carried out at a lower temperature of 250°C. Before actual startup of continuous feeding 37.4 g of tar was put into the reactor manually. The catalyst bed became plugged after 80 minutes in this case.

To improve the effectiveness of hydrogen up-take, and based on the results from the batch trials, it was decided to carry out succeeding tests at a higher pressure of 13.8 MPa (2000 psi). Additionally, a low density, spherical nickel-molybdenum catalyst was chosen (Catalyst F). Run 4 lasted 180 minutes and was stopped voluntarily when the feeder became empty. For the first time, concentrations of methane and carbon dioxide as monitored continuously by gas chromatograph and an infrared analyzer became constant. The run proceeded very smoothly, in general.

During the final stages of depressurizing the reactor, which was still hot, the contents boiled over into the condensers as indicated by a sudden rise in temperature of the first trap. Due to this occurrence, the collected final liquid organic product became contaminated by not fully converted

feed, which usually remained in the reactor after completion of the experiment. The so-called "light distillate" appeared to be more viscous and heavier than in previous runs.

Table 6.6
Gas Analysis from Continuous Runs

	Run Number 4		Run Number 6	
	Grams	Wt % Fed	Grams	Wt % Fed
CO		trace	0.16	0.18
CO ₂	3.53	3.16	7.61	8.41
CH ₄	0.68	0.61	1.66	1.83
C ₂ H ₆	0.22	0.20	0.79	0.87
C ₃ H ₈	0.32	0.29	0.67	0.74
C ₄ +	0.32	0.29	1.18	1.30
	5.07	4.55	12.07	13.33

It was decided for experiment 5 to repeat the previous test but with a different termination procedure. Experiment 5 was ended after 180 minutes with cooling of the system under a hydrogen pressure. The traps this time contained a very light and fluid organic phase on the top of a water phase. It was possible to restart and continue this experiment on the following day. After an additional 180 minutes of

problem-free operation, the pressure regulator became flooded by liquid product and the test was terminated. (This extended portion of the run on the second day is not included in Table 6.5.)

The upgrading test was restarted as Run 6. This time a temperature profile was generated deliberately inside the tubular reactor, roughly in the range recommended by Elliott [9], that is increasing from 240° to 380°C from inlet to outlet of the reactor. Pressure drop across the reactor bed after 2 hours started to fluctuate slightly, and therefore the experiment was stopped voluntarily 30 minutes later. The conditions and yields for all of these six runs are summarized in Table 6.5 and also in Table 6.6. Significant amounts of light distillate were found in the traps so it was decided to apply gas chromatography - mass spectrometry techniques to analyze the liquids obtained.

6.3.4.3 Analysis of Liquid Product by Gas Chromatography - Mass Spectrometry

The analytical equipment and procedures used have been described in previous reports. Graphical representation of the results of the analyses of organic product from experiment 6 is given in Figure 6.5 and the list of tentatively identified compounds is given in Table 6.7.

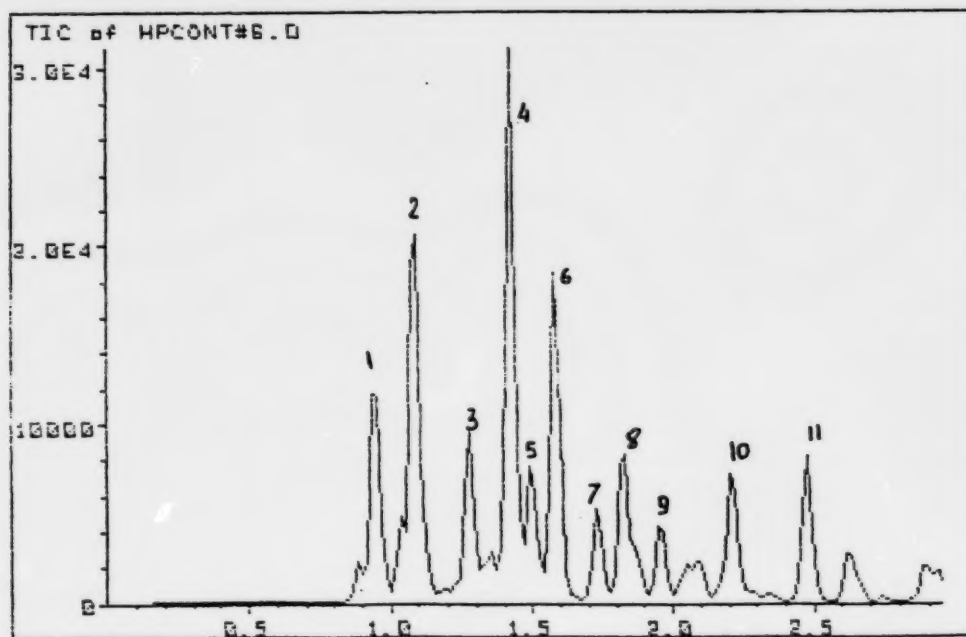
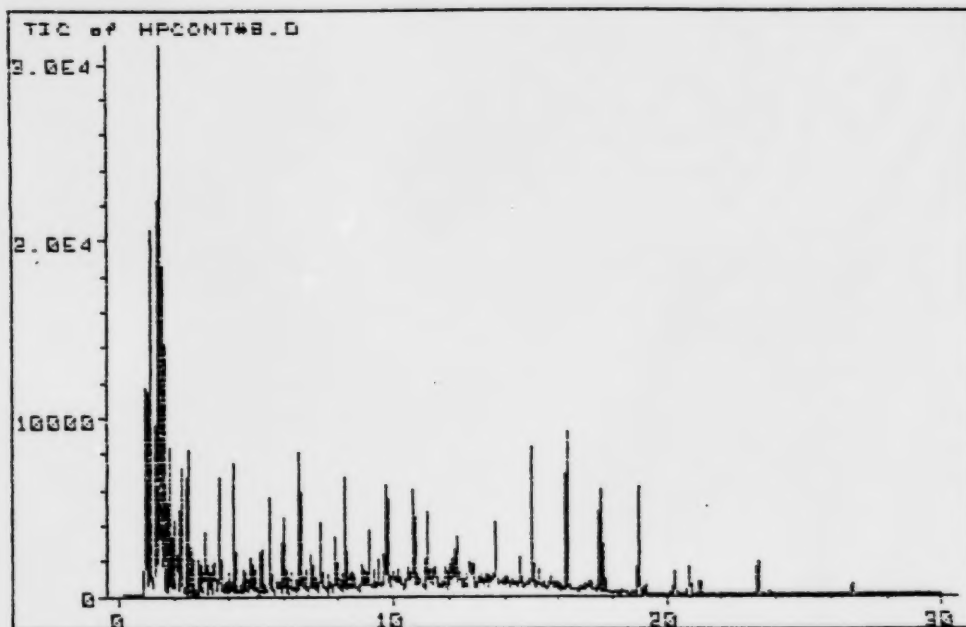


Figure 6.5a GC-MS Results for Analysis of Distillate Product
from Run 6 - Overall Spectra and Low Mass Spectra

Table 6.7

Initial Identification of Liquid Product Components
Run 6, Light Distillate

Peak No.	RT (min.)	Computer Match, % NBS Library	Name
1	0.93	96	Butane
2	1.09	96	Pentane
3	1.23	93	Bicyclo [3,3,1] nonan-2-one, 9-izopropylid
4	1.42	91	Hexane
5	1.49	93	Oxirane, ethyl
6	1.58	96	Cyclopentane, methyl
7	1.72	97	Cyclopentene, 3-methyl
8	1.81	97	Cyclohexane
9	1.99	86	1-Pentyne, 4-methyl
10	2.21	89	Propanoic acid, 2-methylpropyl
11	2.48	98	Cyclohexane, methyl
12	3.11	82	1-Octyne
13	3.67	94	Octane
14	4.20	94	Cyclopentane, 1-methyl-2- (2-propenyl)
15	5.49	97	Undecane
16	5.99	95	Cyclohexane, 2-propenyl
17	6.59	95	Benzenesulfonic acid, 4-hydroxy
18	7.34	96	Isooctane (ethenyloxy)
19	7.86	-	No match above 80%
20	8.24	98	Phenol, 4-methyl
21	9.09	97	Butane, 2, 2-dimethyl
22	9.75	99	Phenol, 4-ethyl
23	10.72	89	Tridecane, 3-methyl
24	11.21	97	Phenol, 2-propyl
25	12.24	97	1-Octanol, 2-Butyl
26	13.68	98	Dodecane, 2-methyl-8-propyl
27	15.03	98	Tridecane
28	16.32	97	Octadecane
29	17.51	98	Dodecane
30	18.99	98	Heptadecane, 9-octyl
31	20.27	-	No match above 80%
32	20.82	98	Tridecane, 7-propyl
33	23.34	99	Docosane
34	26.77	93	Pentadecane

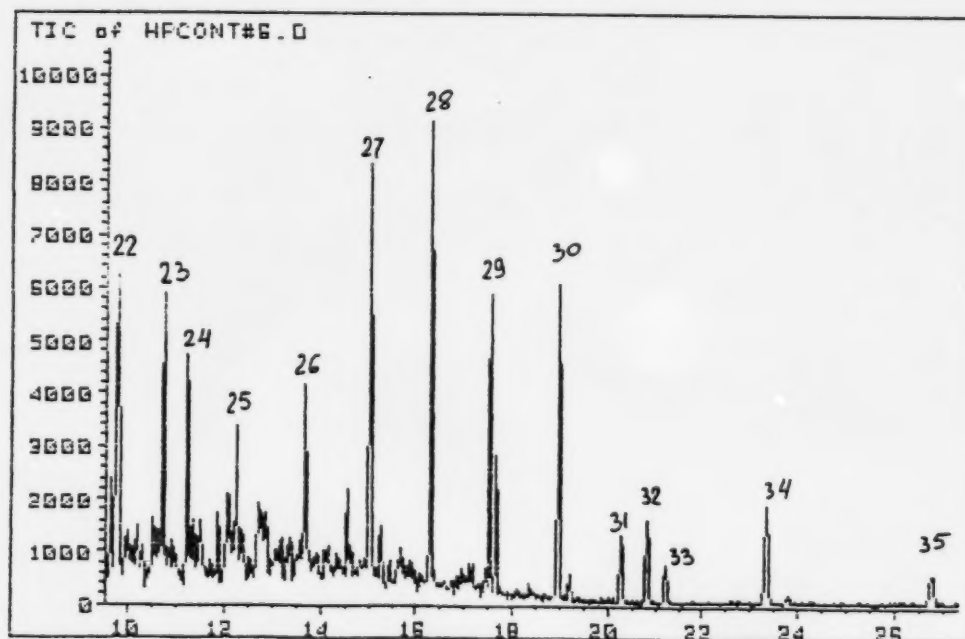
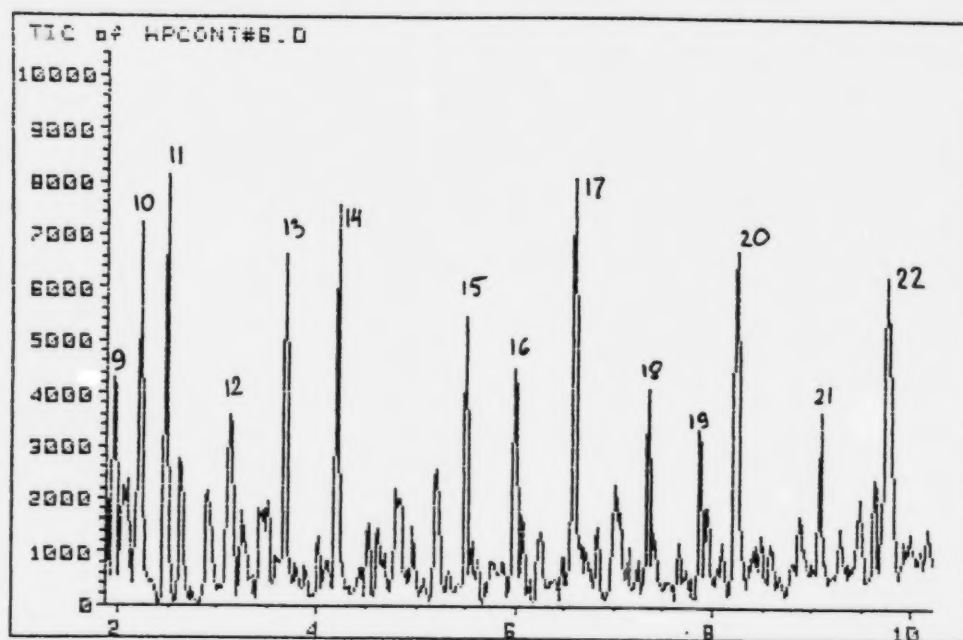


Figure 6.5b GC-MS Results for Analysis of Distillate Product
from Run 6 - Medium Range and High Range Mass Spectra

6.3.4.4 Conclusions

Judging from the GC-MS analysis, the upgrading procedure of Run 6 yielded a similar product to the one reported by Elliott et al. [9]. The major classes of compounds identified are n-alkanes, C_4 to C_6 , cyclopentanes, cyclohexanes and long chain paraffins.

The total yield of light oils of 39% weight as fed is higher than that reported by Elliott et al. [9] (32.9 weight %), but some oxygenated chemicals (phenols) are still visible in the product spectra shown in Figure 6.5 and Table 6.7.

Also, Elliott utilized a different feedstock tar, a different catalyst, and performed his final test in a higher range of temperature (300° to 400°C versus 240° to 380°C). The lower gas yield in our case (13.3% versus 35.4 wt % reported by Elliott et al.) underlines the above stated differences.

6.4 Summary

The experimental laboratory high pressure continuous catalytic rig was successfully set up and tested. Preliminary results seem to confirm the possibility of obtaining a gasoline-like product by upgrading of peat-tar.

This new continuous flow research unit constructed "in-house" for high pressure catalytic studies performed very satisfactorily. It can be considered as an additional and

very useful tool in future studies of the utilization of pyrolysis liquids. In some respects, it is superior to the apparatus used by Elliott. It is believed that the feeding system is simpler and less expensive, and allows the flow rates and volumes of reactor vessels, collectors etc. to be reduced by a factor of about four. Hence, the Waterloo apparatus requires less feed and is more compact and less expensive to build and operate. Also the configuration more nearly approximates plug flow, and this factor, together with our design of heating and cooling coils, makes it easy to establish controlled axial temperature gradients. This feature is necessary to obtain the optimal non-isothermal temperature profile which will result in the desired increasing reaction severity along the flow axis of the reactor.

6.5 Recommendations

The technical expertise obtained during the present work allows us to suggest some improvements which can be implemented in the future:

1. A back pressure regulator should be included in the system (already ordered).
2. There is a need for an additional thermocouple at a fixed position inside the reactor vessel (presently the thermowell gives a movable point of reference for temperature measurement).

3. To be able to better evaluate the hydrogen consumption, an integration device should be connected to the inlet gas mass-flow meter.
4. The differential pressure drop across the bed should be measured directly.
5. A reactor vessel with thicker walls could be constructed and readily installed to allow higher severity processing than is possible presently (400°C, 2000 psi).

6.6 LITERATURE

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6.7 APPENDIX

1. United Catalysts Inc.
2. Katalco Corporation - 499
3. Katalco Corporation - 502-S
4. PUBLICATION - "Production of Liquid Hydrocarbon Fuels from Peat"



United Catalysts Inc.
Girdler and CCI Catalyst
Manufacturers

Typical Chemical and Physical Properties

HYDROTREATING CATALYST

Effective: 5/16/83
Supersedes: 5/12/82

Catalyst Type C20-7-03
Catalyst Form Extrusions
Catalyst Size 1/8" & 1/16"

<u>Chemical Composition</u>	<u>Weight%</u>
NiO*	3.0-4.0
MoO ₃ *	13.0-15.0
P*	1.0-1.5
Al ₂ O ₃	79-84
Other Heavy Metals	<0.20
LOI to Constant Weight at 1000°F*	<5.0

Physical Properties

- A. Bulk Density, lbs./Cu.Ft. 37 ± 3
- B. Surface Area, m²/g* 175-250
- C. Pore Volume, cc/g>29.2 Angstroms* 0.5-0.6
- D. Crush Strength, Lbs. DWL, Min. Avg.*:
 - 1/8" 20.0
 - 1/16" 15.0
- E. Attrition, Wt.% Loss* <5

* Properties normally measured by Quality Control.

KATALCO

499

Product Benefits

- Provides superior DS and good DN
- Higher hydroprocessing activity than cylinders or spheres
- Special shape gives increased liquid holdup
- Contains 15–20% more surface area per unit volume than cylinders or spheres
- Unique shape minimizes pressure drop
- Treats a wide range of feedstocks effectively
- High contaminant metals capacity
- Greater crush strength than other shaped catalysts
- Performs well over a wide range of operating pressures

Feedstocks

- Naphtha
- Kerosene/Diesel
- Gas Oil
- Heavy Vacuum Gas Oil
- Fuel Oil/Cycle Oil
- Hydrocracker Pretreater
- FCC Pretreater

General Description



KATFORM™ 499 is a cobalt-molybdenum catalyst on a shaped alumina base with the following typical properties:

CHEMICAL ANALYSIS WT % DRY BASIS

MoO ₃	19.0%
CoO	4.4%
Alumina	Balance

PHYSICAL PROPERTIES

Form	Shaped Extrudate
Size	Nominal 1/16"
Surface Area, M ² /g	180
Pore Volume, ml/g	0.47
Density (Vibrated), g/ml	0.82
Rx Density, lb/ft ³	47
Crush strength, lb	18
Attrition Index*	98

*% retained on a 20-mesh sieve after tumbling for ½ hour.

Handling

Avoid contact with skin, eyes and clothing. Avoid breathing dust. Do not take internally.

Shipping

KATFORM 499 is available in 55-gallon drums or in 35 cubic foot super sacks. Other packaging requirements can be accom-

modated. Contact your Katalco sales representative about your special requirements.

Katalco

CORPORATION

2809 Butterfield Road • Oak Brook, Illinois 60521 • 312-571-6540 • TELEX: 206793 • KATALCO OB

KATALCO

502-S ✓

Product Benefits

- Excellent DS and DN
- Good saturation activity for olefins and aromatics
- High contaminant metals capacity
- Cost effective choice for reformer pretreater service
- Lower density than extrudate
- High weight activity

Feedstocks

- Naphtha
- Kerosene
- Light cycle oils
- Light gas oils
- Refining gas streams

General Description



SPHERICAT 502-S is a nickel-molybdenum catalyst on a spherical alumina base with the following typical properties:

CHEMICAL ANALYSIS WT % DRY BASIS

MoO ₃	14.0%
NiO	4.0%
Alumina	Balance

PHYSICAL PROPERTIES

Form	Spherical
Size, Nominal	1/8" 1/16"
Surface Area, M ² /g	230 230
Pore Volume, ml/g	0.60 0.60
Density (vibrated), g/ml	0.58 0.58
Rx Density, lb/ft ³	34 34
Crush Strength ¹	18 15
Attrition Index ²	99 99

1. Equivalent side crushing strength of extrudate based on comparative tests with bulk-crush method.

2. Percent retained on a 20-mesh sieve after tumbling for 1/2 hour.

Handling

Avoid contact with skin, eyes and clothing. Avoid breathing dust. Do not take internally.

Shipping

SPHERICAT 502-S is available in 55-gallon drums or in 35 cubic foot super sacks. Other packaging requirements can be accom-

modated. Contact your Katalco sales representative about your special requirements.

Katalco

CORPORATION

2809 Butterfield Road • Oak Brook, Illinois 60521 • 312-571-6540 • TELEX: 206793 • KATALCO OB

Production of Liquid Hydrocarbon Fuels from Peat

Sir: A recent report from the Direct Biomass Liquefaction Cooperative Project (jointly sponsored under the International Energy Agency (IEA), Bioenergy Agreement, by the governments of Canada, Finland, Sweden, and the United States) concluded that atmospheric pressure flash pyrolysis was a cost effective and technically feasible method for the production of liquid fuels from wood and peat.¹ However, further processing of the crude liquid products was needed to produce marketable fuels (gasoline or diesel). Research has progressed rapidly in the case of wood-derived fuels, and two types of processing have now been reported for the production of gasoline-range hydrocarbons from wood pyrolyzates.^{2,3} Peat processing has received less emphasis, but we are now able to report that the conversion of peat to gasoline-range hydrocarbons has been accomplished. The conversion process described in this communication is essentially a two-step process. First, dried peat is pyrolyzed to produce a high yield of tar, and second, the peat tar is catalytically hydrotreated to produce hydrocarbons.

A sample of a young, long fiber, yellow Sogevex sphagnum peat moss (see Table I) from a deposit at Baie-Comeau, Quebec, Canada, was used as the feedstock in the pyrolysis test. Conversion was carried out in the small pilot-plant unit of the Waterloo Fast Pyrolysis process, which has been described in detail elsewhere.⁴ Briefly, pyrolysis was carried out at atmospheric pressure in a fluidized bed of sand, at a feed rate of 1–2 kg/h, with recycled product gas used as the fluidizing agent. Feed particle size, sand size, and fluidization velocity were all chosen so that the peat particle remained well mixed in the sand bed until decomposition reduced the particle density to the point where it was eluted from the bed. Processing parameters and yields are given in Table II. Tar product was recovered from the condensers and from an in-line filter. Details of the product recovery procedure can be found in an earlier publication dealing with the pyrolysis of wood.⁴ The tar is a black, foul-smelling material that is fluid enough to pour at room temperature.

In the catalytic hydrotreating step the crude peat pyrolysis tar (12.3 wt % moisture) was pumped through a nonisothermal catalyst bed with hydrogen to produce hydrocarbons. During this treatment the catalytic hydrotreater at Pacific Northwest Laboratory (as described elsewhere²) was operated in an upflow mode with a catalyst bed of sulfided cobalt–molybdenum on alumina (Harshaw HT 400). The temperature of the bottom of the reactor was held below 300 °C, and the top of the catalyst bed was

Table I. Feedstock and Product Analysis

	Sogevex peat ^a	peat pyroly- zate ^b	hydrotreated product ^b
carbon, wt %	49.5	51.0	84.6
hydrogen, wt %	5.4	7.8	12.8
oxygen, wt %	40.1 ^c	40.3	1.5
nitrogen, wt %	1.3	0.8	1.1
density, g/mL		1.15	0.86

^a Dry basis. ^b As produced (wet basis). ^c By difference.

Table II. Summary of Processing Data

	flash pyrolysis	catalytic hydro- treating
temp, °C	509	302–391
pressure, MPa	0.1	13.8
residence time, sec	0.5	
space velocity, (vol of feed/vol of cat)/h		0.19
liquid product yield, g/g of feed	0.508	0.329
gas product yield, g/g of feed	0.151	0.354
aqueous byproduct yield, g/g of feed	a	0.300
hydrogen consumption, g/g of feed	0	0.036

^a Recovered with the organic liquid product as single phase.

^b Determined by difference of gas feed and outlet gas for the hydrotreater.

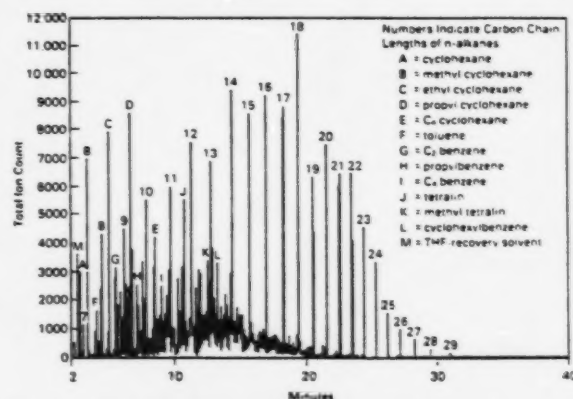


Figure 1. Total ion chromatograph of liquid hydrocarbon product from peat.

near 400 °C. By this type of operation, we were able to control the pyrolytic decomposition of the peat tar and minimize coke formation in the catalyst bed. This nonisothermal operation mimics in one reactor the two-stage hydrotreating that we reported earlier for wood pyrolyzates.²

The results of this test series are encouraging yet far from optimized. The char yield was high in the pyrolysis step (30.4 wt %). Further testing of the relationship of processing severity (reaction temperature and residence time) to product distribution may result in increased liquid and reduced solid product. Gas byproduct is significant in both steps of the process with the main gas being carbon dioxide. Removal of oxygen from the peat is an important aspect of the chemistry, and formation of carbon dioxide is an efficient means for this removal.

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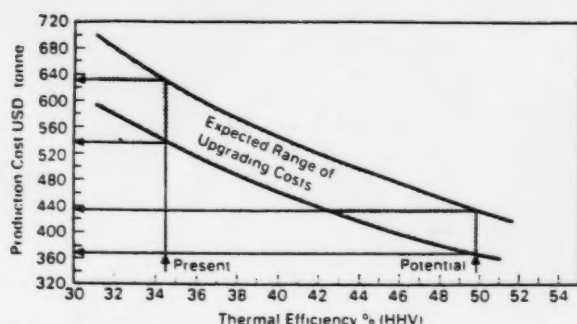


Figure 2. Production cost as a function of energy efficiency.

Analysis of the liquid hydrocarbon product by gas chromatography-mass spectrometry demonstrates the complex nature of hydrocarbons (see Figure 1). The mix of saturated cyclic hydrocarbons and aromatics is similar to that reported earlier for wood-derived products. Small amounts of phenolics, like those reported earlier in wood-derived products, have also been identified. They are remnants of the feedstock that require separation for reprocessing or for use as chemicals. A group of saturated straight-chain hydrocarbons (C_7 - C_{29}) are unique to the peat-derived product and are not produced from wood. They are also reported as present in the peat pyrolysis tar and are apparently derived from waxes that are widely reported to be present in peat. Distillation of the product indicates that 86% is recoverable below 225 °C, the ASTM limit for gasoline boiling range. This fraction contains primarily aromatics and saturated cyclics, which would be good gasoline blending components. The heavier fraction is primarily straight-chain paraffins and might be useful as jet or diesel fuel.

The results of these tests are being used in a preliminary process design analysis as part of the IEA Direct Biomass Liquefaction Cooperative Project. More complete results will be available at a future date. The overall energy efficiency of the process of pyrolysis and hydrotreating is 34.4% based on the higher heating value of the gasoline

product and the peat feedstock. The mass yield is 6526 kg/h gasoline from 41667 kg/h of dry peat in a 1000 ton/day plant. Presently the energy efficiency of the pyrolysis is only 50.3% based on tar yield while the hydrotreatment is only 68.5% energy efficient based on gasoline from tar. Improvements through optimization studies could conceivably increase efficiencies to the 60% range for pyrolysis and 80-85% in the hydrotreatment resulting in an overall process efficiency of about 50%. Efficiency is translated into product cost in Figure 2, which suggests a present price of the gasoline product at about \$600/ton (\$1.74/gallon) and an optimized price of about \$400/ton (\$1.16/gallon) based on an overall process efficiency increased to 50%. These costs are based on a pyrolysis plant cost of \$50 million with a 20-year life and 8% interest. The range of the bar in Figure 2 represents upgrading costs at \$10-20 million/year. Peat feedstock cost is \$16/ton milled peat (50% moisture). As a result, one can conclude that moderate improvements in process efficiency through optimization of the processing parameters can have dramatic effects on the projected cost of product.

Acknowledgment. We thank the Finnish Ministry of Trade and Industry for financial support of this series of experiments.

Registry No. Co, 7440-48-4; Mo, 7439-98-7.

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CAPTIONS

- Figure 3.1 Schematic Diagram of Batch Autoclave Pressure Apparatus for Upgrading of Pyrolytic Oil
- Figure 3.2 Schematic Diagram of Continuous Flow Packed Bed Catalytic Reactor System for Upgrading of Pyrolytic Oil
- Figure 3.3 Detail of Plug Flow Catalytic Reactor
- Figure 3.4 Detail of Feed Inlet of Continuous Catalytic Reactor
- Figure 3.5 a GC-MS Results for Analysis of Distillate Product from Run 6 - Overall Spectra and Low Mass Spectra
- Figure 3.5 b GC-MS Results for Analysis of Distillate Product from Run 6 - Medium Range and High Range Mass Spectra

7. SUMMARY

This initial study of yields of pyrolytic liquids from Canadian peat has shown that good yields of organic liquids can be obtained with the Waterloo Fast Pyrolysis Process from younger peats. In addition, it has been demonstrated that a fluidized bed of the same general design as the pyrolysis reactor can be used very successfully to pre-dry peat before pyrolysis, if this is desired.

When peat which has been milled to a size less than 2 mm is fed to a fluid bed filled with sand and which is fluidized by hot gas or oil, this peat can be rapidly dried to a low moisture content, e.g. to less than 5%. The fluid bed dryer operates in the same manner as the WFPP pyrolysis reactor, that is, in the "blow-through" mode. Fluidizing gas velocity, sand particle size and feed particle size are pre-selected so that wet peat particles remain in the bed, but as the density of the particle decreases due to moisture loss, the particle is ultimately eluted from the bed and recovered as dry peat in the product cyclone.

The great bulk of the water content of younger peats (long or short fibred yellow or brown peat) can be removed in a constant rate drying period. Critical moisture content is about 10% to 12%. As a result, if the peat is not overdried, the particle will not be heated significantly above the adiabatic saturation temperature, and thus will undergo a minimum of irreversible thermal structural change.

Constant drying rates measured with bed temperatures from 90°C to 115°C were in the range of 0.5 to 0.8 kg moisture per kg dry peat per minute (as deduced from TGA results) with initial moisture contents from 0.4 to 0.8 kg moisture/kg dry peat. Although drying rates were not measured in the fluidized bed, they appear from approximate estimates to be as high or higher than the TGA values. Good heat balances ($\pm 5\%$) were obtained using the pilot plant fluidized bed, lending support to the above conclusions. If air is used as the drying gas, a maximum temperature of about 300°C at the inlet is suggested to avoid fire hazard.

Thermal gravimetric tests of wet peat can give useful preliminary results on drying behaviour and drying rates for unknown peat samples.

Pyrolysis of a Quebec Sogevex peat in an atmospheric pressure fluidized bed reactor was studied in some detail in pilot plant tests. A rather broad flat maximum yield of organic liquid of 45% to 48% mf feed was obtained in the range from 460° to 550°C. Product water yields varied from 7% to 10% with no clear trend. Char yields decreased steadily from 35% at 450°C to about 25% at 700°C, while gas yield increased steadily from 12% to 38% over the same temperature range.

The nature of the liquid product showed a distinct change with respect to the amount of water soluble components over the temperature range of 450° to 550°C. Above 550°C, the ratio of

water soluble/water insoluble product remained approximately constant. However, at 460°C, this ratio was about 2.3, while at 550°C, it was about 0.6. This change in liquid character probably reflects the easier decomposition of cellulose, or cellulose and hemicellulose degradation products, in the peat at low temperatures to yield oxygenated aliphatic compounds or sugars. At higher temperatures, the lignin related components of the peat would decompose to yield aromatic compounds. In sphagnum peats, the only lignin-like precursor is sphagnol, which on pyrolysis gives rise to non-methoxylated alkyl phenols. In addition to the carbohydrate-derived and lignin-derived decomposition products, the tars from peat pyrolysis also contain significant amounts of long chain alcohols and ketones which would not be water soluble. The GC-MS results for the tar from Run 102 (550°C) show the presence of C₉ to C₂₀ hydrocarbons as major components. This fraction represents the "wax" sometimes recovered commercially.

Gas yields tend to follow the same pattern as that observed in biomass pyrolysis, that is, large amounts of CO₂ are produced at low temperatures but the yield plateaus at about 550°C at around 10%. The amount of the other major gas component, CO, rises steadily from about 3% at 450°C to 20% at 700°C. From 450° to 550°C, these two gases account for 89% to 94% by weight of the total gas yield. Above 550°C, the amount of light hydrocarbon gases increases rapidly, with olefins in particular increasing from about 1% at 550°C to 3.6% at 692°C.

Two major sugars derived from the carbohydrate fraction, presumably from cellulose, gave the highest yields at the lowest temperatures, with about 9% levoglucosan and 1.7% cellobiosan at 450°C, which represents about a 47% yield based on cellulose content of the peat. The decrease in yield of these two components with temperature represents about 50% of the decrease in water soluble products already mentioned.

Elemental analysis of char and tar products showed a steadily decreasing H/C ratio for chars and a nearly constant H/C ratio for tars over the temperature range from 460° to 692°C. Over the range of 460° to 550°C, the oxygen content of the oil fell from about 39% to 34%, which reflects the decrease in water soluble oxygenated components as temperature increased. The incremental oxygen appears to be rejected, as temperature increases, primarily as CO, and the decrease in tar yield from 550° to 692°C is accounted for largely by the increase in CO yield plus increased additional smaller amounts of hydrocarbon gases. At 692°C, the tar contains only about 26.5% oxygen, but it is also fairly high in nitrogen (2.5%).

Thermogravimetric analysis of peat is able to give a reasonable indication of probable yield of tars, but it is not a particularly accurate method and could not be considered to be reliable for quantitative estimates.

Moisture content of the peat in the range of 5% to 30% by weight did not affect product yields significantly. A twofold variation in feed rate also had no effect on product yield. The char from peat tends to retain the shape of the original feed particle, similar to biomass particles when pyrolyzed.

Comparison of our results to results reported in the literature for yields of organic liquids from peats is somewhat difficult for two reasons, first, much of the reported work does not fit our definition of "fast" pyrolysis, and was not intended to maximize liquid yields and second, much of the work was done on low grade peats which would be expected to give lower yields of organic volatiles. The exhaustive review of Roy et al. (1983) reports many results from the large body of Russian work, for which the highest reported yields of tar appear to be 20% to 30% of the dry peat feed with a maximum of 42% from a young peat. Roy (1980) for vacuum pyrolysis reported a maximum total liquid yield of 49% of the dry ash-free peat which may be compared to the 58% maximum yield obtained in our work from a slightly higher grade of peat than used by Roy. Duncan et al. (1981) reported yields from the IGT Hyflex process by hydropyrolysis of a sedge (*Carex*) type peat of about 22.9% of the feed carbon at 600°C and 200 psig H₂ pressure, vs. a conversion of 44% of the carbon fed in Sogevex peat to organic liquid in this work. Very little of the reported work on peat pyrolysis has used residence times of less than about 5 seconds. As a result, liquid yields were generally reduced. In

another report, Duncan et al. (1980) using a twin fluidized bed dryer and pyrolyzer with steam or nitrogen as fluidizing gases and a low grade peat feedstock obtained maximum liquid yields of 30%, or 20% of organic liquids. In summary, the Waterloo Fast Pyrolysis Process appears to give liquid yields from any grade of peat which are as good as, or better than, those obtained by other processes.

Upgrading studies of the WFPP peat oil were carried out originally in a batch autoclave. However, the thermally sensitive nature of pyrolysis oils requires a special non-isothermal hydrogenation-deoxygenation sequence. Initially a mild treatment is desired to stabilize the oil, presumably by destruction of the most reactive groups such as aldehydes, followed by a more severe deoxygenation treatment. It was found difficult to control this process in a stirred autoclave so a continuous plug flow reactor was constructed. This unit was modeled after that described by Elliott but was smaller, required less feed, and was much less expensive to construct and operate. It yielded very good results with a sulfided nickel-molybdenum on alumina catalyst, giving a gasoline-like product from a whole peat tar in a yield of about 18.3% of the original dry peat. This value was slightly higher than that reported by Elliott et al. (1988).

8. CONCLUSIONS

The major conclusions which arise from the studies reported here are listed below in point form for brevity.

1. A variety of types of peats can be successfully dried in a sand filled fluidized bed at atmospheric pressure. For all but highly decomposed black peats, the bulk of the water can be removed in a constant rate period, with the peat particles not being heated significantly above the adiabatic saturation temperature. Drying rates in the fluidized bed are high.
2. Yellow or brown peats, short or long fibred, can be pyrolyzed readily in a fluidized bed at atmospheric pressure by the Waterloo Fast Pyrolysis Process.
3. Maximum yields of organic liquids from a Quebec brown peat were 48% by weight of the moisture free feed. Corresponding gas and char yields were about 13% and 30%, respectively.
4. The yield of organic liquids was nearly constant at 45% to 48% over the temperature range 460° to 550°C. However, the character of the liquid changed over this temperature span with a steadily decreasing amount of water soluble product, and an increasing amount of water insoluble product.
5. Yields of organic liquids were not affected significantly by moisture content to 30%; by changes in feed rate of a factor or two; or by minor changes ($\pm 20\%$) in residence time of vapour.

6. The quality of the organic liquid product changed with temperature increase to a decreasing oxygen content, although the H/C ratio stayed approximately constant. The decrease in tar yields above 550°C was due largely to CO formation plus minor increases in hydrocarbon gas yields.
7. In addition to the same kind of oxygenated pyrolysis products found in pyrolysis tars from cellulosic biomass, which are derived from cellulose and hemicellulose, the peat tar also contained aromatic alkyl phenols without methoxy groups derived from sphagnol, and long chain paraffins and their derivatives.
8. In general, the yields from the pilot plant pyrolysis tests on the Quebec sphagnum peat moss were entirely comparable to the yields obtained in our earlier study on pyrolysis of a Finnish fuel grade peat using the bench scale fluidized bed reactor.
9. Both drying rate behaviour and pyrolysis yield behaviour for peats can be rapidly and semi-quantitatively established by thermogravimetric analysis.
10. Organic liquid yields from a low grade black fuel grade Quebec peat were somewhat lower than those from brown peat (40% mf vs. 47% mf) with corresponding increases in char yield. However, considering the difference in peat quality, yields of pyrolysis products were surprisingly similar.

11. Peat oil can be upgraded by high pressure catalytic deoxygenation/hydrogenation to give a gasoline range liquid with a yield of about 18% of the peat fed (mf), or about 38% of the peat oil produced.
12. An improved continuous plug flow fixed bed catalytic reactor for upgrading studies has been designed and successfully tested.

9. RECOMMENDATIONS

The results and conclusions presented in the previous sections of this report suggest strongly two additional avenues of further study that would be worthwhile. These are embodied in the two major recommendations below.

- a) Pyrolysis studies should be carried out on additional low grade (that is, highly decomposed) peats in order to evaluate liquid yields, quality of the char, and the necessary process conditions. These fuel grade peats are presently not produced commercially, so that the test materials used should be carefully chosen to be representative of deposits which might be used as a fuel energy source in the relatively near future. Drying of these peats may also present more difficulties, and this aspect should also be investigated. Much research has been done on peat drying, and other processes may be more suitable for the drying of these lower grade peats.
- b) If possible, the yields of some of the major components of pyrolysis tar which are unique products of peat pyrolysis should be quantitatively measured. This time-consuming task would be worthwhile only in conjunction with upgrading experiments, or in connection with market evaluations of the peat oil.

- c) Some combustion tests of the whole peat oil should be undertaken. This would require larger quantities of oil, and should be done in collaboration with a commercial producer of peat products.
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10. REFERENCES

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11. APPENDIX

Heat Balance Example -
Pilot Plant Log Sheet Sample

Heat Balance Example

In order to carry out the heat balance, the following basic balance equation can be written.

$$\begin{aligned} & \text{Heat entering in air above datum} + \text{heat entering in feed} \\ = & \text{Heat loss from reactor} + \text{heat required to heat wet peat to} \\ & \text{exit temperature} + \text{heat required to evaporate water at} \\ & \text{exit temperature} + \text{heat leaving in exit dry air} + \text{heat leaving in dry peat} \end{aligned}$$

If the datum is chosen to be room temperature (21°C) then one of the the above terms can be omitted.

Other data required

Specific heat of peat = 0.4 cal/gK (estimated - see Sect. 4.1.3)

Heat loss can be calculated from Run 1, Table 4.3

C_{pair} (mean from 21° - 100°C) = 0.24 cal/g K

Heat loss (Run 1)

Gas flow rate = 100 l/min , 21°C , 1 atm

Density of air at 21°C , 1 atm = 1.202 g/l

Temperature of bed = 162°C

Exit temperature of air = 149°C

$$\text{Therefore Heat loss} = \left(\frac{100}{60} \right) (1.202) (0.24)(162-149) = 6.25 \text{ cal/s}$$

The mean temperature difference between reactor and ambient is

$$\left(\frac{162 + 149}{2} \right) - 21 = 135$$

$$\text{Therefore Heat loss rate from reactor} = \frac{6.25}{135} = 0.046 \text{ cal/Ks}$$

Heat Balance Calculation - Run 12 as an Example (Table 4.4)

Heat into reactor in air = 100 l/min (21°, 1 atm) at 277

$$= 2.0033 \text{ g/s of air}$$

$$= (2.0033) (0.24) (277 - 21) = 123.1 \text{ cal/s}$$

Heat exiting from reactor (exit temperature 150°C, Bed temperature 157°)

Heat out as heat loss

$$= (0.046) (153-21) = 6.1 \text{ cal/s}$$

Moisture in peat entering 0.8 kg/kg dry peat

Moisture in peat leaving 0.004 kg/kg

Peat feed rate 0.308 kg dry/hr

$$\text{Moisture evaporated} = (0.8 - 0.004) \left(\frac{0.308}{3600} \right) (1000) = 0.0681 \text{ g/s}$$

Heat leaving in peat = heat in dry peat + heat to heat H₂O

to 150 C + latent heat at 150 C

$$= \left(\frac{308}{3600} \right) (0.4) (150-21) + (0.0684) (0.95) (150-21)$$

$$+ (0.0681) (505) = 4.41 + 8.38 + 34.39 = 47.2 \text{ cal/s}$$

Heat leaving in dry air at 150°C (115 l/min, 21°C, 1 atm)

$$= (2.0033) \left(\frac{115}{100} \right) (0.24) (150-21) = 71.3 \text{ cal/s}$$

$$\text{Total Heat Out} = 47.2 + 71.3 + 6.1 = 124.6 \text{ cal/s}$$

$$\text{Heat in} = 123.1 \text{ cal/s}$$

$$\text{Difference} = \underline{1.2\%}$$

Humidity of inlet air = 0.0025 kg/kg dry air (Sect 4.1.2)

Humidity of exit air = 0.0681 gm/s evaporated/2.304 gm/s dry air

$$+ 0.0025 = 0.032 \text{ kg H}_2\text{O/kg dry air}$$

Dry bulb temperature at exit = 150°C Adiabatic Saturation temp. = 50°C

Pilot Plant Log Sheet IRun No. 88Date: Sept. 24/861. Feed Sogevex% Moisture 25.4 % Ash 3.7

Elemental Analysis (maf)

XC _____ XH _____ XN _____

Particle Size _____

2. Objective3. Time Started 0Time Ended 114 MinutesTemperature Readings C

Time (min)	before	3	8	15	25	35	45	55	65	75	85	95	105
Furnace Top	794	798	796	796	795	795	795	795	795	795	797	795	795
Pleum	624	711	700	695	692	692	692	692	692	693	693	692	691
Fluid Bed	537	580	562	553	552	556	546	552	553	550	554	555	554
Reactor top	483	526	521	514	512	515	509	515	516	516	518	520	520
Hot Condenser	47	55	56	57	58	60	61	61	63	64	66	67	68
Cold Condenser	2	constant		+	+	+	+	+	+	+	+	+	+
Orifice	27	"											

Pressure Readings, inches H₂O

Time	before	8	15	25	35	45	55	65	75	85	95	105
Reactor, ΔP	30	+++ constant										
Reactor, P	50	+++ "										
Cyclone	4.5	+++ "										
Hot Condenser	1	1	1	1	1	1.2	1.5	1.5	1.5	1.7	1.8	2
Cold Condenser	11	15	18	24	28	28	28	26	26	30	30	30
Hopper-Reactor, ΔP	30	37 + constant										
Compressor Outlet, P	200	+++ constant										
Orifice, ΔP	80	70 ++ constant										
Orifice, P	190	++++ "										
Cotton Filter	40	50	52	55	56	64	80	88	92	96	94	89

Pilot Plant Log Sheet IIRun No. 88Date: Sept. 24/86

Product Gas Composition (Anarad) % Vol.

Time	8	16	25	35	38	45	55	65	75	85	95	105	110	114
CO ₂	8	10	12	13	14	16	17	18		22			25	
CO	1	3	5	6	7	9	10	11		16			20	

Feed charged to hopper 3078.6 grams.Feed remaining in hopper 1451.3 grams.Amount Fed 1627.3 grams; 0.86 kgs/hr.

Collected Condensate	Weight, grams	Volume, ml.
Hot Condenser	<u>-</u>	<u> </u>
Cold Condenser	<u>537</u>	<u> </u>
Total, both Condensers	<u> </u>	<u> </u>
Condensate from filter trap	<u> </u>	<u> </u>
Total Condensate (Liquor)	<u> </u>	<u> </u>
Tar in filters - cotton	<u>375.4</u>	<u> </u>
Tar from the washing	<u> </u>	<u> </u>
+ solvent evaporation	<u>176</u>	<u> </u>
Total Tar	<u> </u>	<u> </u>

Char from char pot 307.8 gramsChar from solvent wash 8.8 gramsTotal Char 316.6Total Product Gas Volume (wet test meter) 140 litresFinal Product Gas Composition, Vol. % N₂ freeH₂ 2.11; CO 39.09; CO₂ 47.03; CH₄ 7.34; C₂H₄ 2.37; C₂H₆ 0.58;C₃ 0.64; C₄ 0.45; N₂ zero

Pilot Plant Log Sheet IIIRun No. 88Date: Sept. 24/86Summary of Results

	Weight, grams	Weight % of Feed	Weight %, maf
Liquor	537	33.0	
Tar	551.4	33.88	
Char	316.6	19.46	
Gas	203.1	12.49	
Total Recovery	1608.1	98.82	

Water Content (Karl Fischer)

Liquor _____ % by weight; _____ grams of water

Tar _____ % by weight; _____ grams of water

Final Balance

	<u>Grams</u>	<u>Wt % of Feed</u>	<u>Wt % maf</u>
Gas	203.1	12.49	16.73
Char	316.6	19.46	26.08
Water	465.8	28.62	4.32
Organics	623.4	38.31	51.35
Totals	1608.9	98.88	98.48

Summary of Elemental Analysis, % by Weight

	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>
Liquor (incl. water)				
Tar (incl. water)				
Char				